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(54) Lubricating oil compositions, concentrates and the use thereof.

(57) Oleaginous compositions and additive concentrates therefor having enhanced performance characteristics comprise at least a) one or more oil-soluble metal dihydrocarbyl dithiophosphates or dithiocarbamates; and b) one or more oil-soluble additive compositions formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing; or (ii) at least one water-hydrolyzable organic phosphorus compound and water; and (iii) at least one boron compound; such that a phosphorus- and boron-containing liquid composition is formed, and from which excessive water, if present, has been removed at least during or after heating with (ii), if used.

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## Lubricating oil compositions, concentrates and the use thereof.

Description of EP0493928

### TECHNICAL FIELD

This invention relates to oleaginous compositions of enhanced performance characteristics, to additive concentrates for enhancing the performance characteristics of oleaginous base fluids (e.g., lubricants and functional fluids), and to methods of achieving such enhanced performance characteristics.

### BACKGROUND

Over the years the demand for performance improvements in lubricating oils and functional fluids has persisted and, if anything, progressively increased. For example, lubricating oils for use in internal combustion engines, and in particular, in spark-ignition and diesel engines, are constantly being modified and improved to provide improved performance. Various organizations including the SAE (Society of Automotive Engineers), the ASTM (formerly the American Society for Testing Materials) and the API (American Petroleum Institute) as well as the automotive manufacturers continually seek to improve the performance of lubricating oils. Various standards have been established and modified over the years through the efforts of these organizations. As engines have increased in power output and complexity, and in many cases decreased in size, the performance requirements have been increased to provide lubricating oils that will exhibit a reduced tendency to deteriorate under conditions of use and thereby to reduce wear and the formation of such undesirable deposits as varnish, sludge, carbonaceous materials and resinous materials which tend to adhere to various engine parts and reduce the operational efficiency of the engine.

Current objectives include the development of additive formulations and lubricant compositions, especially crankcase lubricants and crankcase lubricant additive packages, capable of achieving these stringent performance requirements without requiring use of increased amounts of metal-containing components, such as zinc dihydrocarbyl dithiophosphates. Indeed, if possible, it is desired to achieve these stringent performance requirements with reduced amounts of such metal-containing components. Still another desirable objective is to provide additive formulations and lubricant compositions which exhibit good compatibility with elastomeric substances utilized in the manufacture of seals, gaskets, clutch plate facings, and like parts. Unfortunately, commonly used additives containing basic nitrogen constituents tend to cause excessive degradation of such elastomers when oils containing such additives come in contact with such elastomers during actual service conditions.

There are literally hundreds, if not thousands, of patent disclosures describing attempts (some more successful than others) to improve the performance characteristics of oils of lubricating viscosity. A small selection from this vast body of literature comprises U.S. 3,087,936; 3,184,411; 3,185,645; 3,235,497; 3,254,025; 3,265,618; 3,281,428; 3,282,955; 3,284,410; 3,324,032; 3,325,567; 3,338,832; 3,344,069; 3,403,102; 3,502,677; 3,511,780; 3,513,093; 3,533,945; 3,623,985; 3,718,663; 3,865,740; 3,950,341; 3,991,056; 4,097,389; 4,234,435; 4,338,205; 4,428,849; 4,554,086; 4,615,826; 4,634,543; 4,648,980; 4,747,971; 4,857,214; and 4,873,004.

### THE INVENTION

This invention provides additive systems capable of imparting enhanced performance characteristics to natural and synthetic oils of lubricating viscosity. In addition, this invention makes it possible to achieve such enhanced performance with additive systems containing reduced amounts of metal-containing performance enhancers such as metal dithiophosphates and/or metal dithiocarbamates. In short, this invention makes it possible to achieve a high level of performance with a reduced level of conventional metal-containing performance enhancers such as zinc dialkyldithiophosphates.

In accordance with this invention there is provided in one of its embodiments a composition comprising a major proportion of at least one oil of lubricating viscosity and a minor proportion of at least the following components:

- one or more oil-soluble metal hydrocarbyl dithiophosphates or dithiocarbammates; and
- one or more oil-soluble additive compositions formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at

least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing; or (ii) at least one water-hydrolyzable organic phosphorus compound and water; and (iii) at least one boron compound; such that a liquid composition is formed. In the formation of such liquid composition from (ii) and (iii), water is removed at least during or after the heating with (ii) and (iii) (if conducted concurrently) or at least during or after the heating with (ii) (if conducted sequentially).

The cooperation between components a) and b) of such compositions makes it possible to achieve performance levels (reduction in sludge formation and/or deposition and reduction in wear in gears and/or other relatively moveable metal surfaces in contact with each other) normally achieved, if at all, by higher concentrations of component a). Moreover, these performance levels can be maintained for long periods of time despite the well-known relatively low thermal stability of compounds such as the zinc dihydrocarbyl dithiophosphates.

Another advantageous feature of this invention is that certain preferred combinations of components a) and b) can exhibit good compatibility toward elastomers commonly employed in the manufacture of seals or gaskets, clutch plate facings, etc., such as nitrile rubbers, fluoroelastomers, and silicone-type elastomers. In other words, such elastomers are not subjected to excessive degradation when in contact under actual service conditions with a preferred lubricant or functional fluid composition of this invention containing particular combinations of components a) and b), which combinations are thus preferred because of this advantageous characteristic which they possess and exhibit in the base oil. To realize these advantageous characteristics, component b) should be formed from one or more sulfur-free phosphorus compounds and the overall sulfur content of the finished lubricant or functional fluid composition should be kept below about 1% and most preferably below about 0.3% based on the total weight of the finished lubricant or functional fluid composition.

Another embodiment of this invention involves the discovery, inter alia, that basic alkali metal-containing and/or basic alkaline earth metal-containing detergents of the types generally known to be useful in oleaginous fluids (e.g., overbased sulfonates, overbased phenates, overbased sulfurized phenates, overbased salicylates, overbased sulfurized salicylates, etc.) can serve a dual role in the compositions of this invention. Besides contributing detergency to the compositions, such metal compounds can serve to reduce corrosive attack on so-called "yellow metals" such as copper, bronze, and the like. Detergents of the foregoing types having a total base number (TBN) of at least about 50 are utilized in the practice of this embodiment of the invention. In this connection, TBN is determined in accordance with ASTM D-2896-88.

Accordingly, another embodiment of this invention is a composition comprising a major proportion of at least one oil of lubricating viscosity and a minor proportion of at least the following components:

- a) one or more oil-soluble metal hydrocarbyl dithiophosphates or dithiocarbamates;
- b) one or more oil-soluble additive compositions formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing; or (ii) at least one water-hydrolyzable organic phosphorus compound and water; and (iii) at least one boron compound; such that a liquid phosphorus- and boron-containing composition is formed; and
- c) one or more oil-soluble alkali or alkaline earth metal-containing detergents having a TBN of at least about 50. When b) is formed from (ii) and (iii), water is removed at some stage during or after the heating with at least (ii).

Additive concentrates comprising at least components a) and b) above, and preferably additionally containing component c), i.e., one or more suitably basic, oil-soluble alkali metal-containing and/or alkaline earth metal-containing detergents, constitute additional embodiments of this invention.

Among the preferred embodiments of this invention are oleaginous compositions and additive concentrates in which component a) is at least one oil-soluble metal hydrocarbyl dithiophosphate (preferably a zinc hydrocarbyl dithiophosphate and most preferably a zinc dialkyl dithiophosphate), and in which the relative proportions of components a) and b) are such that the atom ratio of phosphorus in the form of component a) to phosphorus in the form of component b), respectively, falls in the range of about 10:1 to about 0.01:1 (and more preferably in the range of about 5:1 to about 0.1:1 and most preferably in the range of about 4:1 to about 1:1). Particularly preferred are compositions of these types which additionally contain component c) in an amount such that the atom ratio of total metal in the form of component a) to total metal in the form of component c), respectively, falls in the range of about 0.01:1 to about 10:1 (and more preferably in the range of about 0.1:1 to about 4:1). Especially preferred are lubricants and functional fluids containing components a), b), and c) proportioned as specified in this paragraph wherein the total content of metals in the form of components a) and c) is in the range of about 0.01 to about 3, preferably in the range of about 0.05 to about 1.8, and most preferably in the range of about 0.1 to about 1.0 weight percent of metals based on the total weight of the lubricant composition or

functional fluid composition. Despite their low level of "ash" or metal-containing components, such lubricant and functional fluid compositions can provide a high level of performance.

In order to satisfy the stringent specification requirements to qualify for top-grade crankcase lubricating oils, it is necessary to include in the compositions of this invention a combination of antioxidant and corrosion inhibitor. In this way, the enhanced performance (e.g., effective control of sludge, deposit and varnish formation and of wear of contacting metal parts) made possible by this invention can be maintained while at the same time satisfying specification requirements associated with oxidation and corrosion inhibition. Thus in another preferred embodiment of this invention, there is provided a crankcase lubricant composition which comprises a major proportion of at least one oil of lubricating viscosity and a minor proportion of at least the following components:

- a) one or more oil-soluble metal hydrocarbyl dithiophosphates or dithiocarbamates;
- b) one or more oil-soluble additive compositions formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing — preferably one or more sulfur-free inorganic phosphorus acids; most preferably phosphorous acid ( $H_3PO_3$ ); or (ii) at least one water-hydrolyzable organic phosphorus compound and water — preferably one or more halogen-free boron compounds; most preferably boric acid and/or one or more boric acid esters; and (iii) at least one boron compound — preferably one or more halogen-free boron compounds; most preferably boric acid and/or one or more boric acid esters; such that a liquid composition is formed;
- c) one or more oil-soluble alkali or alkaline earth metal-containing detergents having a TBN of at least about 50, preferably above 100, more preferably above 200, and most preferably above 300;
- d) one or more oil-soluble antioxidants; and
- e) one or more oil-soluble corrosion inhibitors; such that said lubricant composition satisfies (1) the requirements of the Sequence IID, Sequence IIIE, and Sequence VE procedures of the American Petroleum Institute; and/or (2) the requirements of the L-38 Test Procedure of the American Petroleum Institute; and/or (3) the requirements of the Caterpillar TM 1G(2) and/or the 1H(2) Test Procedure.

Additional preferred embodiments of this invention involve providing oleaginous compositions and additive compositions in which the amount of phosphorus present in the form of component b) is equal to or in excess of the amount of phosphorus present in the form of component a). Thus for example, in accordance with this embodiment, preferred are compositions in which the atom ratio of phosphorus in the form of component a) to phosphorus in the form of component b), respectively, falls in the range of about 0.001:1 to 1:1, more preferably in the range of about 0.01:1 to 0.99:1, and most preferably in the range of about 0.1:1 to about 0.95:1.

Among the most preferred embodiments of this invention are oleaginous fluids wherein component a) is composed of one or more oil-soluble zinc dihydrocarbyl dithiophosphates, wherein components a) and b) are proportioned such that the atom ratio of phosphorus in the form of component a) to phosphorus in the form of component b), respectively, falls in the range of about 4:1 to about 1:1, and wherein the phosphorus content of such fluids is in the range of about 0.05 to about 0.15% by weight of the total composition, especially where such fluids additionally contain at least one oil-soluble alkali or alkaline earth metal-containing detergent having a TBN of at least 50, preferably above 100, more preferably above 200, and most preferably above 300.

Other embodiments of this invention include the provision of methods for inhibiting sludge formation and/or deposition in oils normally tending to occur during actual service conditions, and methods for imparting antiwear and/or extreme pressure properties to oils of lubricating viscosity.

The above and other embodiments and features of this invention will become further apparent from the ensuing description and appended claims.

#### Component a)

In essence, there are two general categories of additives which may be used singly or in combination with each other as component a) in the practice of this invention. One type of such additives is comprised of oil-soluble metal hydrocarbyl dithiophosphates. The other is comprised of oil-soluble metal hydrocarbyl dithiocarbamates.

#### Type 1 - Metal hydrocarbyl dithiophosphates.

As is well known, metal hydrocarbyl dithiophosphates are usually prepared by reacting phosphorus

pentasulfide with one or more alcohols or phenolic compounds or diols to produce a hydrocarbyl dithiophosphoric acid which is then neutralized with one or more metal-containing bases. When a monohydric alcohol or phenol is used in this reaction, the final product is a metal dihydrocarbyl dithiophosphate. On the other hand, when a suitable diol (e.g., 2,4-pentanediol) is used in this reaction, the final product is a metal salt of a cyclic hydrocarbyl dithiophosphoric acid. See, for example, U.S. Pat. No. 3,089,850. Thus typical oil-soluble metal hydrocarbyl dithiophosphates used as component a) may be represented by the formula EMI8.1 where R<sub>1</sub> and R<sub>2</sub> are, independently, hydrocarbyl groups or taken together are a single hydrocarbyl group forming a cyclic structure with the phosphorus and two oxygen atoms, preferably a hydrocarbyl-substituted trimethylene group of sufficient carbon content to render the compound oil soluble, M is a metal, and x is an integer corresponding to the valence of M. The preferred compounds are those in which R<sub>1</sub> and R<sub>2</sub> are separate hydrocarbyl groups (i.e., the metal dihydrocarbyl dithiophosphates). Usually the hydrocarbyl groups of the metal dihydrocarbyl dithiophosphates will contain no more than about 50 carbon atoms each although even higher molecular weight hydrocarbyl groups can be present in the compound. The hydrocarbyl groups include cyclic and acyclic groups, both saturated and unsaturated, such as alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, cycloalkylalkyl, aralkyl, and the like. It will be understood that the hydrocarbyl groups may contain elements other than carbon and hydrogen provided such other elements do not detract from the predominantly hydrocarbonaceous character of the hydrocarbyl group. Thus the hydrocarbyl groups may contain ether oxygen atoms, thioether sulfur atoms, secondary or tertiary amino nitrogen atoms, and/or inert functional groups such as esterified carboxylic groups, keto groups, thioketo groups, and the like.

The metals present in the oil-soluble metal dihydrocarbyl dithiophosphates and oil-soluble metal cyclic hydrocarbyl dithiophosphates include such metals as lithium, sodium, potassium, copper, magnesium, calcium, zinc, strontium, cadmium, barium, mercury, aluminum, tin, lead, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, ruthenium, etc., as well as combinations of two or more such metals. Of the foregoing, the salts containing group II metals, aluminum, lead, tin, molybdenum, manganese, cobalt, and/or nickel, are preferred. The dihydrocarbyl dithiophosphates of zinc and copper are particularly preferred, with the zinc salts being the most preferred type of compound for use as component a).

The phosphorodithioic acids from which the metal salts are formed can be prepared by the reaction of about 4 moles of one or more alcohols (cyclic or acyclic) or one or more phenols or mixture of one or more alcohols and one or more phenols (or about 2 moles of one or more diols) per mole of phosphorus pentasulfide, and the reaction may be carried out within a temperature range of from about 50 to about 200 DEG C. The reaction generally is completed in about 1 to 10 hours. Hydrogen sulfide is liberated during the reaction.

Another method for the preparation of the phosphorodithioic acids involves reaction of one or more alcohols and/or one or more phenols with phosphorus sesquisulfide in the presence of sulfur such as is described in PCT International Publication No. WO 90/07512. This reaction is conducted at an elevated temperature, preferably in the range of 85-150 DEG C with an overall atomic P:S ratio of at least 2.5:1.

The alcohols used in forming the phosphorodithioic acids by either of the above methods are preferably primary alcohols, or secondary alcohols. Mixtures thereof are also suitable. The primary alcohols include propanol, butanol, isobutyl alcohol, pentanol, 2-ethyl-1-hexanol, isoctyl alcohol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, octadecanol, eicosanol, and the like. The primary alcohols may contain various substituent groups such as halogen atoms, nitro groups, etc., which do not interfere with the desired reaction. Among suitable secondary alcohols are included 2-butanol, 2-pentanol, 3-pentanol, 2-hexanol, 5-methyl-2-hexanol, and the like. In some cases, it is preferable to utilize mixtures of various alcohols, such as mixtures of 2-propanol with one or more higher molecular weight primary alcohols, especially primary alcohols having from 4 to about 13 carbon atoms in the molecule. Such mixtures preferably contain at least 10 mole percent of 2-propanol, and usually will contain from about 20 to about 90 mole percent of 2-propanol. In one preferred embodiment, the alcohol comprises about 30 to 50 mole percent of 2-propanol, about 30 to 50 mole percent isobutyl alcohol and about 10 to 30 mole percent of 2-ethyl-1-hexanol.

Other suitable mixtures of alcohols include 2-propanol/butanol; 2-propanol/2-butanol; 2-propanol/2-ethyl-1-hexanol; butanol/2-ethyl-1-hexanol; isobutyl alcohol/2-ethyl-1-hexanol; and 2-propanol/tridecanol.

Cycloaliphatic alcohols suitable for use in the production of the phosphorodithioic acids include cyclopentanol, cyclohexanol, methylcyclohexanol, cyclooctanol, borneol and the like. Preferably, such alcohols are used in combination with one or more primary alkanols such as butanol, isobutyl alcohol, or the like.

Illustrative phenols which can be employed in forming the phosphorodithioic acids include phenol, o-cresol, m-cresol, p-cresol, 4-ethylphenol, 2,4-xylenol, and the like. It is desirable to employ phenolic compounds in combination with primary alkanols such as propanol, butanol, hexanol, or the like.

Other alcohols which can be employed include benzyl alcohol, cyclohexenol, and their ring-alkylated analogs.

It will be appreciated that when mixtures of two or more alcohols and/or phenols are employed in forming the phosphorodithioic acid, the resultant product will normally comprise a mixture of three or more different dihydrocarbyl phosphorodithioic acids, usually in the form of a statistical distribution in relation to the number and proportions of alcohols and/or phenols used.

Illustrative diols which can be used in forming the phosphorodithioic acids include 2,4-pentanediol, 2,4-hexanediol, 3,5-heptanediol, 7-methyl-2,4-octanediol, neopentyl glycol, 2-butyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, and the like.

The preparation of the metal salts of the dihydrocarbyl dithiophosphoric acids or the cyclic hydrocarbyl dithiophosphoric acids is usually effected by reacting the acid product with a suitable metal compound such as a metal carbonate, metal hydroxide, metal alkoxide, metal oxide, or other appropriate metal salt. Simply mixing and heating such reactants is normally sufficient to cause the reaction to occur and the resulting product is usually of sufficient purity for use in the practice of this invention. Typically, the salts are formed in the presence of a diluent such as an alcohol, water or a light mineral oil. Neutral salts are prepared by reacting one equivalent of metal oxide or hydroxide with one equivalent of the acid. Basic metal salts are prepared by adding an excess (i.e., more than one equivalent) of the metal oxide or hydroxide with one equivalent of the dihydrocarbyl phosphorodithioic acid or cyclic hydrocarbyl phosphorodithioic acid.

Illustrative metal compounds which may be used in such reactions include calcium oxide, calcium hydroxide, silver oxide, silver carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate, magnesium ethoxide, zinc oxide, zinc hydroxide, strontium oxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, cadmium carbonate, barium oxide, aluminum oxide, aluminum propoxide, iron carbonate, copper hydroxide, lead oxide, tin butoxide, cobalt oxide, nickel hydroxide, manganese oxide, and the like.

In some cases, incorporation of certain ingredients such as small amounts of metal acetate or acetic acid in conjunction with the metal reactant will facilitate the reaction and provide an improved product. For example, use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide tends to facilitate the formation of zinc dihydrocarbyl dithiophosphates.

Examples of useful metal salts of dihydrocarbyl dithiophosphoric acids, and methods for preparing such salts are found in the prior art such as for example, U.S. Pat. Nos. 4,263,150; 4,289,635; 4,308,154; 4,322,479; 4,417,990; and 4,466,895.

Generally speaking, the preferred types of metal salts of dihydrocarbyl dithiophosphoric acids are the oil-soluble metal salts of dialkyl dithiophosphoric acids. Such compounds generally contain alkyl groups having at least three carbon atoms, and preferably the alkyl groups contain up to 10 carbon atoms although as noted above, even higher molecular weight alkyl groups are entirely feasible. A few illustrative zinc dialkyl dithiophosphates include zinc diisopropyl dithiophosphate, zinc dibutyl dithiophosphate, zinc diisobutyl dithiophosphate, zinc di-sec-butyl dithiophosphate, the zinc dipentyl dithiophosphates, the zinc dihexyl dithiophosphates, the zinc diheptyl dithiophosphates, the zinc dioctyl dithiophosphates, the zinc dinonyl dithiophosphates, the zinc didecyl dithiophosphates, and the higher homologs thereof. Mixtures of two or more such metal compounds are often preferred for use such as metal salts of dithiophosphoric acids formed from mixtures of isopropyl alcohol and secondary butyl alcohol; isopropyl alcohol, isobutyl alcohol, and 2-ethylhexyl alcohol; isopropyl alcohol, butyl alcohol, and pentyl alcohol; isobutyl alcohol and octyl alcohol; and the like.

If desired, the metal dihydrocarbyl dithiophosphate additives of the type described above may be treated with an epoxide to form an adduct. In general, the most suitable metal dihydrocarbyl dithiophosphates useful in forming such adducts are the zinc dihydrocarbyl dithiophosphates. The epoxides comprise alkylene oxides and arylalkylene oxides. Typical alkylene oxides which may be used include alkylene oxides having up to about 8 carbon atoms in the molecule, such as ethylene oxide, propylene oxide, 1,2-butene oxide, trimethylene oxide, tetramethylene oxide, butadiene monoepoxide, 1,2-hexene oxide, epichlorohydrin, and the like. The arylalkylene oxides are exemplified by styrene oxide. Other suitable epoxides include, for example, butyl 9,10-epoxystearate, epoxidized soybean oil, epoxidized tung oil, and epoxidized styrene-butadiene copolymer. Procedures for preparing epoxide adducts are known and are reported, for example, in U.S. Pat. No. 3,390,082.

The adduct may be obtained by simply mixing the metal phosphorodithioate and the epoxide. The reaction is usually exothermic and may be carried out within wide temperature limits from about 0 DEG C to about 300 DEG C. Because the reaction is exothermic, it is best carried out by adding one reactant, usually the

epoxide, in small increments to the other reactant in order to obtain convenient control of the temperature of the reaction. The reaction may be carried out in a solvent such as benzene, mineral oil, naphtha, or n-hexene.

The chemical structure of the adduct is not known. The adducts obtained by the reaction of one mole of the phosphorodithioate with from about 0.25 mole to 5 moles, usually up to about 0.75 mole or about 0.5 mole of a lower alkylene oxide, particularly ethylene oxide and propylene oxide, are the preferred adducts.

Another type of metal dihydrocarbyl phosphorodithioate additives contemplated as useful as component a) in the compositions of this invention comprises mixed-acid metal salts of a combination of (a) at least one phosphorodithioic acid of the formula  $(RO)(R\text{ min }O)\text{PSSH}$ , as exemplified above ( $R$  and  $R\text{ min}$  being, independently, hydrocarbyl groups (or taken together, a single hydrocarbyl group forming a cyclic moiety with the two oxygen atoms and the phosphorus atom) of sufficient carbon content to render the salt soluble in lubricating oil), and (b) at least one aliphatic or alicyclic carboxylic acid. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3 carboxy groups and preferably only one. It may contain from about 2 to about 40, preferably from about 2 to about 20 carbon atoms, and advantageously about 5 to about 20 carbon atoms. The preferred red carboxylic acids are those having the formula  $R<3>\text{COOH}$ , wherein  $R<3>$  is an aliphatic or alicyclic hydrocarbon-based radical preferably free from acetylenic unsaturation. Suitable acids include the butanoic, pentanoic, hexanoic, octanoic, nonanoic, decanoic, dodecanoic, octadecanoic and eicosanoic acids, as well as olefinic acids such as oleic, linoleic, and linolenic acids and linoleic acid dimer. For the most part,  $R<3>$  is a saturated aliphatic group and especially a branched alkyl group such as the isopropyl or 3-heptyl group. Illustrative polycarboxylic acids are succinic, alkyl- and alkenylsuccinic, adipic, sebacic and citric acids.

The mixed-acid metal salts may be prepared by merely blending a metal salt of a phosphorodithioic acid with a metal salt of a carboxylic acid in the desired ratio. The ratio of equivalents of phosphorodithioic to carboxylic acid salts is between about 0.5:1 and about 200:1. Advantageously, the ratio can be from about 0.5:1 to about 100:1, preferably from about 0.5:1 to about 50:1, and more preferably from about 0.5:1 to about 20:1. Further, the ratio can be from about 0.5:1 to about 4.5:1, preferably about 2.5:1 to about 4.25:1. For this purpose, the equivalent weight of a phosphorodithioic acid is its molecular weight divided by the number of -PSSH groups therein, and that of a carboxylic acid is its molecular weight divided by the number of carboxy groups therein.

A second and preferred method for preparing the mixed-acid metal salts useful in this invention is to prepare a mixture of the acids in the desired ratio and to react the acid mixture with a suitable metal base. When this method of preparation is used, it is frequently possible to prepare a salt containing an excess of metal with respect to the number of equivalents of acid present; thus, mixed-acid metal salts containing as many as two equivalents and especially up to about 1.5 equivalents of metal per equivalent of acid may be prepared. The equivalent of a metal for this purpose is its atomic weight divided by its valence.

Variants of the above-described methods may also be used to prepare the mixed-acid metal salts useful in this invention. For example, a metal salt of either acid may be blended with an acid of the other, and the resulting blend reacted with additional metal base.

Suitable metal bases for the preparation of the mixed-acid metal salts include the oxides, hydroxides, alkoxides and other basic salts of the metals previously enumerated, and in some cases the free metals themselves. Examples are sodium hydroxide, potassium hydroxide, magnesium oxide, calcium hydroxide, zinc oxide, lead oxide, nickel oxide and the like.

The temperature at which the mixed-acid metal salts are prepared is generally between about 30 DEG C and about 150 DEG C, preferably up to about 125 DEG C. If the mixed-acid salts are prepared by neutralization of a mixture of acids with a metal base, it is preferred to employ temperatures above about 50 DEG C and especially above about 75 DEG C. It is frequently advantageous to conduct the reaction in the presence of a substantially inert, normally liquid organic diluent such as naphtha, benzene, xylene, mineral oil and the like. If the diluent is mineral oil, it frequently need not be removed before using the mixed-acid metal salt as an additive for lubricants or functional fluids.

U.S. Patents 4,308,154 and 4,417,970 describe procedures for preparing these mixed-acid metal salts and disclose a number of examples of such mixed salts.

#### Type 2 - Metal hydrocarbyl dithiocarbamates.

The second type of oil-soluble metal salts used as component a) in the compositions of this invention are salts of one or more dithiocarbamic acids of the formula  $\text{RR min N-CSSH}$  wherein  $R$  and  $R\text{ min}$  are each

independently hydrocarbyl groups in which the total number of carbon atoms in R and R min is sufficient to render the metal salt oil-soluble. R and R min taken together may represent a polymethylene or alkyl substituted polymethylene group thereby forming a cyclic compound with the nitrogen atom (i.e., a monocyclic hydrocarbyl dithiocarbamate). Generally the hydrocarbyl groups will each contain at least two carbon atoms and may contain 50 or more carbon atoms. The metal component present in the dihydrocarbyl (or monocyclic hydrocarbyl) dithiocarbamate salts may be a monovalent metal or a polyvalent metal, although polyvalent metals are preferred as the salts of the polyvalent metals tend to possess better solubility in oils of lubricating viscosity. Thus although the alkali metal monocyclic hydrocarbyl or dihydrocarbyl dithiocarbamates may be used if oil-soluble, the preferred salts include, for example, salts of one or more of the alkaline earth metals, zinc, cadmium, magnesium, tin, molybdenum, iron, copper, nickel, cobalt, chromium, lead, etc. The Group II metal dihydrocarbyl dithiocarbamates are preferred.

In selecting a metal salt of a dithiocarbamic acid to be used in the compositions of this invention, R, R min, and the metal may be varied so long as the metal salt is adequately oil-soluble. The nature and type of the mineral base stock, and the type of service contemplated for the treated lubricating oil should be taken into consideration in the choice of metal salt.

The metal constituent of the metal dihydrocarbyl dithiocarbamate is usually a simple metal cation. However in the case of certain polyvalent metal derivatives such as the tin and lead compounds, the metal constituent itself may be hydrocarbyl substituted (e.g., (RR min N-CSS-)xMR1R2, where M is a polyvalent metal, R, R min, R1 and R2 are, independently, hydrocarbyl groups (and, optionally R and R min taken together are a single cyclic hydrocarbyl group) in which the total number of carbon atoms is sufficient to render the compound oil-soluble, and x is an integer sufficient to satisfy the remaining valence(s) of M. Techniques described for example in U.S. Pat. No. 2,786,814, may be employed for preparing such hydrocarbyl-substituted metal dithiocarbamates.

Mixtures of metal salts of dithiocarbamic acids also are contemplated as being useful in the present invention. Such mixtures can be prepared by first preparing mixtures of dithiocarbamic acids and thereafter converting said acid mixtures to metal salts, or alternatively, metal salts of various dithiocarbamic acids can be prepared and thereafter mixed to give the desired product. Thus, the mixtures which can be incorporated in the compositions of the invention may be merely the physical mixture of the different metallic dithiocarbamic compounds, or compounds having different dithiocarbamate groupings attached to the same polyvalent metal atoms.

Examples of alkyl groups are ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, decyl, dodecyl, tridecyl, pentadecyl and hexadecyl groups including isomeric forms thereof. Examples of cycloalkyl groups include cyclohexyl and cycloheptyl groups, and examples of aralkyl groups include benzyl and phenethyl. Examples of polymethylene groups include penta- and hexamethylene groups, and examples of alkyl-substituted polymethylene groups include methyl pentamethylene, dimethyl pentamethylene, etc.

Specific examples of the metal dithiocarbamates useful as component a) in the compositions of this invention include zinc dibutyl dithiocarbamate, zinc diamyl dithiocarbamate, zinc di(2-ethylhexyl) dithiocarbamate, cadmium dibutyl dithiocarbamate, cadmium dioctyl dithiocarbamate, cadmium octylbutyl dithiocarbamate, magnesium dibutyl dithiocarbamate, magnesium dioctyl dithiocarbamate, cadmium dicetyl dithiocarbamate, copper diamyl dithiocarbamate, sodium dioctadecyl dithiocarbamate, lead dioctyl dithiocarbamate, nickel diheptyl dithiocarbamate, calcium di-2-ethylhexyl dithiocarbamate, etc.

The various metal salts of dithiocarbamic acids utilized in the compositions of this invention are well known in the art and can be prepared by known techniques. See for example Ullmann, Encyklopädie der technischen Chemie, Band 10, Verlag Chemie, Weinheim, copyright 1975, pages 167-170 (and references cited therein); Thorn and Ludwig, The Dithiocarbamates and Related Compounds, Elsevier Publishing Company, 1962, pages 12 to 37 (and references cited therein); Delepine, Compt. Rend., 144, 1125 (1907); Whitby et al, Proceedings and Transactions of The Royal Society of Canada, XVIII, 111-114 (1924) (and references cited therein), Chabrier et al, Bulletin de la Societe Chimique De France, 1950, pages 43 et seq. (and references cited therein), and U.S. Pat. Nos. 1,622,534; 1,921,091; 2,046,875; 2,046,876; 2,258,847; 2,406,960; 2,443,160; 2,450,633; 2,492,314; 2,580,274; 3,513,094; 3,630,897; 4,178,258; and 4,226,733.

While boron is not a metallic element, boron tris(dihydrocarbyl dithiocarbamates) can be used as component a) of the compositions of this invention, either individually or in combination with one or more metal dihydrocarbyl dithiocarbamates. Methods suitable for the production of such boron dithiocarbamates are set forth in U.S. Pat. No. 4,879,071.

Derivatives of metal dihydrocarbyl dithiocarbamates may be used in addition to or in lieu of the metal dihydrocarbyl dithiocarbamates. Such derivatives include dithiocarbamatederived phosphates such as are described in U.S. Pat. No. 4,919,830, reaction products of N,N-diorganodithiocarbamates with thionyl

chloride such as are described in U.S. Pat. No. 4,867,893, N,N-diorganodithiocarbamate-alkylthiosulfinyl halide reaction products such as are described in U.S. Pat. No. 4,859,356, reaction products of halogenated EPDM terpolymers and alkali metal dialkyldithiocarbamate such as are described in U.S. Pat. No. 4,502,972, and sulfurized metal dihydrocarbyl dithiocarbamates such as are described in U.S. Pat. No. 4,360,438, among others. In addition, the metal dihydrocarbyl dithiocarbamates may be used in combination with other carbamate compounds such as for example, a 1,2-dicarbethoxyethyl dialkyldithiocarbamate such as is disclosed in U.S. Pat. No. 4,479,883; or a mercaptoalkanoic acid dithiocarbamate of the type described in U.S. Pat. No. 3,890,363.

Mixtures of different metal dihydrocarbyl dithiocarbamates as well as combinations of (1) one or more metal dihydrocarbyl dithiophosphates and (2) one or more metal dihydrocarbyl dithiocarbamates can be used as component a) in the practice of this invention.

#### Component b)

The other indispensable additive ingredient of the compositions of this invention is comprised of one or more oil-soluble additive compositions formed by heating concurrently or any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one inorganic phosphorus acid or anhydride or at least one partial or total sulfur analog thereof, or any combination of the foregoing; or (ii) at least one water-hydrolyzable organic compound of phosphorus – preferably a water-hydrolyzable ester of an acid of phosphorus – and water; and (iii) at least one boron compound, such that a liquid phosphorus- and boron-containing composition is formed, and from which water has been removed when (ii) and (iii) are used. The ashless dispersant which is heated concurrently or in any sequence with components (i) or (ii) and (iii) is preferably a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group. Thus, for example, any suitable ashless dispersant formed in the customary manner can be heated with one or more boron compounds to cause boronation to occur and the resultant product mixture can then be heated with (i) one or more inorganic phosphorus compounds or (ii) one or more water-hydrolyzable organic phosphorus compounds and water, such that a liquid phosphorus- and boron-containing composition [component b)] is formed. Conversely, a preformed ashless dispersant can be heated with (i) one or more inorganic phosphorus compounds or (ii) one or more water-hydrolyzable organic phosphorus compounds and water, and thereafter the product mixture can be heated with one or more boron compounds so that a liquid phosphorus- and boron-containing composition is formed. The preferred way of forming component b) is to heat a preformed ashless dispersant with a combination of one or more inorganic phosphorus compounds and one or more boron compounds to form a liquid phosphorus- and boron-containing composition. In other words, to form component b) in the preferred manner, the preformed ashless dispersant is concurrently heated with one or more inorganic phosphorus compounds and one or more boron compounds. In all cases, the resulting liquid product composition when subjected to chemical analysis reveals the presence of both phosphorus and boron.

Rather than utilizing a preformed ashless dispersant containing basic nitrogen and/or at least one hydroxyl group, it is possible to produce component b) by:

- 1) forming the ashless dispersant in the presence of one or more suitable boron compounds (e.g., boron ester or boron oxide) and then heating the resultant composition with (i) one or more inorganic phosphorus compounds or (ii) one or more water-hydrolyzable organic phosphorus compounds and water; or
- 2) forming the ashless dispersant in the presence of (i) one or more suitable inorganic phosphorus compounds (e.g., a phosphorus oxide or sulfide) and then heating the resultant composition with one or more boron compounds, or forming the ashless dispersant in the presence of (ii) one or more water-hydrolyzable organic phosphorus compounds and then heating the resultant composition with one or more boron compounds in the presence of water; or
- 3) forming the ashless dispersant in the presence of one or more suitable boron compounds (see 1) above) and one or more suitable inorganic phosphorus compounds (see 2) above); or forming the ashless dispersant in the presence of one or more boron compounds and one or more water-hydrolyzable organic phosphorus compounds and heating the ashless dispersant in the presence of water either during or after the formation of the ashless dispersant; or
- 4) heating one or more boron compounds with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, using the resultant boronated reactant to form the ashless dispersant and then heating the resultant ashless dispersant with (i) one or more inorganic phosphorus compounds or (ii) with one or more water-hydrolyzable organic phosphorus compounds in the presence of water; or
- 5) heating (i) one or more inorganic phosphorus compounds or (ii) one or more water-hydrolyzable organic phosphorus compounds in the presence of water, with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, using the resultant phosphorylated reactant to form the ashless dispersant and then heating the resultant ashless dispersant with one or more boron compounds; or

6) heating (i) one or more inorganic phosphorus compounds and one more boron compounds or (ii) in the presence of water one or more water-hydrolyzable organic phosphorus compounds and one more boron compounds, with a basic nitrogen-containing and/or hydroxyl group-containing reactant used in forming the ashless dispersant, and using the resultant phosphorylated and boronated reactant to form the ashless dispersant.

In all cases, the final product composition [component b)] should be a liquid composition that on analysis reveals the presence of boron and phosphorus. Such product composition should also exhibit dispersant properties. In any case wherein an ashless dispersant used in forming component b) is not a liquid but rather is in whole or in part in the solid state of aggregation at room temperature (e.g., 25 DEG C), it is preferable to dissolve such dispersant in a suitable solvent or diluent (polar or non-polar, as may be required to dissolve the dispersant) before the dispersant is subjected to phosphorylation and/or boronation (as the case may be) in forming component b). In this connection, the phrase "such that a liquid composition is formed" as used herein in connection with such solid state dispersants means that component b), including such solvent or diluent, is in the liquid state of aggregation at room temperature (e.g., 25 DEG C), even though at a lower temperature the dispersant may revert in whole or in part to the solid state. Of course in any case, component b) must be oil-soluble within the meaning of such term as set forth hereinafter.

Irrespective of the method used in forming component b), in any instance wherein macro (i.e., non-dispersible) solids are formed or remain in the liquid composition after it has been formed, such solids should be removed, and can be readily removed, by any of a variety of conventional separation techniques such as filtration, centrifugation, decantation, or the like.

The actual chemical structures of the final product compositions used as component b) in the practice of this invention, however prepared, are not known with absolute certainty. While it is believed that phosphorus-containing moieties and boron-containing moieties are chemically bonded to the ashless dispersant, it is possible that component b) is in whole or in part a micellar structure containing phosphorus- and/or boron-containing species or moieties. Thus, this invention is not limited to, and should not be construed as being limited to, any specific structural configurations with respect to component b). As noted above, all that is required is that component b) is a liquid that is oil soluble and that if subjected to analysis reveals the presence of both phosphorus and boron. In addition, component b) should possess dispersant properties.

Although any of a variety of standard methods can be used to analyze the phosphorylated and boronated dispersant for the presence of phosphorus and boron therein, it is desirable to use the analytical procedure set forth in ASTM D4951. In this procedure it is convenient to use a Perkin-Elmer Plasma 40 Emission Spectrometer. The analyzing wavelengths for acceptable measurements are 213.618 nm and 249.773 nm for phosphorus and boron, respectively.

The phosphorylated and boronated dispersants utilized as component b) in the compositions of this invention when in their undiluted state should have on a weight basis a phosphorus content of at least 100 parts per million (ppm) (preferably at least 500 ppm and more preferably at least 1000 ppm) and a boron content of at least 100 ppm (preferably at least 500 ppm and more preferably at least 1000 ppm).

It is to be understood and appreciated that component b) may contain chemical species and/or moieties besides the phosphorus- and boron-containing species or moieties such as, for example, nitrogen- and/or oxygen- and/or sulfur-containing species or moieties over and above the basic nitrogen and/or hydroxyl group(s) forming an essential part of the initial ashless dispersant itself. It is also to be understood and appreciated that organic phosphorus-containing compounds may be used along with inorganic phosphorus compounds in making component b). Further, the inorganic phosphorus compound or compounds can be formed in situ, as, for example, by heating a mixture of phosphorus and sulfur to form a phosphorus sulfide, or by treating one or more organic phosphorus compounds to convert the same in whole or in part into one or more inorganic phosphorus compounds. Also, inorganic phosphorus-containing compounds may be used along with water and one or more water-hydrolyzable organic phosphorus compounds in making component b). Further, the water-hydrolyzable organic phosphorus compound or compounds can be formed in situ, as, for example, by heating a mixture of one or more alcohols or phenols with one or more phosphorus halides (e.g., PCl<sub>3</sub>, POCl<sub>3</sub>, PSCl<sub>3</sub>, RPCl<sub>2</sub>, ROPOCl<sub>2</sub>, RSPCl<sub>2</sub>, RPOCl<sub>2</sub>, ROPOCl<sub>2</sub>, RSPOCl<sub>2</sub>, RPSCI<sub>2</sub>, ROPSCI<sub>2</sub>, RSPSCI<sub>2</sub>, R<sub>2</sub>PCl, (RO)<sub>2</sub>PCl, (RS)<sub>2</sub>PCl, (RO) (RS) PCl, R<sub>2</sub>POCl, (RO)<sub>2</sub>POCl, (RS)<sub>2</sub>POCl, (RO) (RS) POCl, R<sub>2</sub>PSCI, (RO)<sub>2</sub>PSCI, (RS)<sub>2</sub>PSCI, etc., where each R is, independently, a hydrocarbyl group) and introducing water into the system in order to hydrolyze the water-hydrolyzable phosphorus ester so formed.

As used herein, the term "phosphorylated" means that the ashless dispersant has been heated with (i) one or more inorganic phosphorus compounds or with (ii) one or more water-hydrolyzable organic phosphorus compounds and water, such that the resultant product, on analysis, reveals the presence of phosphorus. Likewise, as used herein, the term "boronated" means that the ashless dispersant has been heated with

one or more boron compounds such that the resultant product, on analysis, reveals the presence of boron. As noted hereinabove, the precise chemical makeup of the phosphorylated and boronated dispersant compositions is not known with absolute certainty. Thus the terms "phosphorylated" and "boronated" are not to be construed as requiring that the resultant composition contain chemically bound phosphorus or boron. While it is believed that chemical reactions do occur to produce a composition containing at least some chemically bound phosphorus moieties and at least some chemically bound boron moieties, moieties or species of either or both of such elements conceivably could be present, at least in part, in the form of micellar structures.

Any of a variety of ashless dispersants can be utilized in forming component b) of the compositions of this invention. These include the following types:

#### Type A - Carboxylic Dispersants.

These products are described in many patents, including British patent specification No. 1,306,529 and the following U.S. Patents: 3,163,603; 3,184,474; 3,215,707; 3,219,666; 3,271,310; 3,272,746; 3,281,357; 3,306,908; 3,311,558; 3,316,177; 3,340,281; 3,341,542; 3,346,493; 3,381,022; 3,399,141; 3,415,750; 3,433,744; 3,444,170; 3,448,048; 3,448,049; 3,451,933; 3,454,607; 3,467,668; 3,522,179; 3,541,012; 3,542,678; 3,574,101; 3,576,743; 3,630,904; 3,632,510; 3,632,511; 3,697,428; 3,725,441; 3,868,330; 3,948,800; 4,234,435; and Re 26,433.

There are a number of sub-categories of carboxylic dispersants. One such sub-category which constitutes a preferred type for use in the formation of component b) is composed of the polyamine succinamides and more preferably the polyamine succinimides in which the succinic group contains a hydrocarbyl substituent containing at least 30 carbon atoms. The polyamine used in forming such compounds contains at least one primary amino group capable of forming an imide group on reaction with a hydrocarbon-substituted succinic acid or acid derivative thereof such as anhydride, lower alkyl ester, acid, halide, or acid-ester. Representative examples of such dispersants are given in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with a polyamine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of olefin and maleic anhydride to about 180 DEG -220 DEG C. The olefin is preferably a polymer or copolymer of a lower monoolefin such as ethylene, propylene, 1-butene, isobutene and the like. The more preferred source of alkenyl group is from polyisobutene having a number average molecular weight of up to 100,000 or higher. In a still more preferred embodiment the alkenyl group is a polyisobutetyl group having a number average molecular weight (determined using the method described in detail hereinafter) of about 500-5,000, and preferably about 700-2,500, more preferably about 700-1,400, and especially 800-1,200. The isobutene used in making the polyisobutene is usually (but not necessarily) a mixture of isobutene and other C4 isomers such as 1-butene. Thus, strictly speaking, the acylating agent formed from maleic anhydride and "polyisobutene" made from such mixtures of isobutene and other C4 isomers such as 1-butene, can be termed a "polybutenyl succinic anhydride" and a succinimide made therewith can be termed a "polybutenyl succinimide". However, it is common to refer to such substances as "polyisobutetyl succinic anhydride" and "polyisobutetyl succinimide", respectively. As used herein "polyisobutetyl" is used to denote the alkenyl moiety whether made from a highly pure isobutene or a more impure mixture of isobutene and other C4 isomers such as 1-butene.

Polyamines which may be employed in forming the ashless dispersant include any that have at least one primary amino group which can react to form an imide group. A few representative examples include branched-chain alkanes containing two or more primary amino groups such as tetraamino-neopentane, etc.; polyaminoalkanols such as 2-(2-aminoethylamino)-ethanol and 2-[2-(2-aminoethylamino)-ethylamino]-ethanol; heterocyclic compounds containing two or more amino groups at least one of which is a primary amino group such as 1-(beta-aminoethyl)-2-imidazolidone, 2-(2-aminoethylamino)-5-nitropyridine, 3-amino-N-ethylpiperidine, 2-(2-aminoethyl)-pyridine, 5-aminoindole, 3-amino-5-mercaptop-1,2,4-triazole, and 4-(aminomethyl)-piperidine; and the alkylene polyamines such as propylene diamine, dipropylene triamine, di-(1,2-butylene)triamine, N-(2-aminoethyl)-1,3-propanediamine, hexamethylenediamine and tetra-(1,2-propylene)pentamine.

The most preferred amines are the ethylene polyamines which can be depicted by the formula H<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>NH)<sub>n</sub>H wherein n is an integer from one to about ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and the like, including mixtures thereof in which case n is the average value of the mixture. These ethylene polyamines have a primary amine group at each end so can form mono-alkenylsuccinimides and bis-alkenylsuccinimides. Commercially available ethylene polyamine mixtures usually contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N min -bis(aminoethyl)

piperazine, N,N min -bis(piperazinyl)ethane, and like compounds. The preferred commercial mixtures have approximate overall compositions falling in the range corresponding to diethylene triamine to pentaethylene hexamine, mixtures generally corresponding in overall makeup to tetraethylene pentamine being most preferred. Methods for the production of polyalkylene polyamines are known and reported in the literature. See for example U.S. Pat. No. 4,827,037 and references cited therein.

Thus especially preferred ashless dispersants for use in the present invention are the products of reaction of a polyethylene polyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon-substituted carboxylic acid or anhydride (or other suitable acid derivative) made by reaction of a polyolefin, preferably polyisobutene, having a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400 and especially 800 to 1,200, with an unsaturated polycarboxylic acid or anhydride, e.g., maleic anhydride, maleic acid, fumaric acid, or the like, including mixtures of two or more such substances.

As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between the amine reactant(s) and the hydrocarbon-substituted carboxylic acid or anhydride (or like acid derivative) reactant(s), and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

Residual unsaturation in the alkenyl group of the alkenyl succinimide may be used as a reaction site, if desired. For example the alkenyl substituent may be hydrogenated to form an alkyl substituent. Similarly the olefinic bond(s) in the alkenyl substituent may be sulfurized, halogenated, hydrohalogenated or the like. Ordinarily, there is little to be gained by use of such techniques, and thus the use of alkenyl succinimides as the precursor of component b) is preferred.

Another sub-category of carboxylic dispersants which can be used in forming component b) includes alkenyl succinic acid esters and diesters of alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups. Representative examples are described in U.S. Pat. Nos. 3,331,776; 3,381,022; and 3,522,179. The alkenyl succinic portion of these esters corresponds to the alkenyl succinic portion of the succinimides described above including the same preferred and most preferred subgenus, e.g., alkenyl succinic acids and anhydrides, etc., where the alkenyl group contains at least 30 carbon atoms and notably, polyisobutetyl succinic acids and anhydrides wherein the polyisobutetyl group has a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400, and especially 800 to 1,200. As in the case of the succinimides, the alkenyl group can be hydrogenated or subjected to other reactions involving olefinic double bonds.

Alcohols useful in preparing the esters include methanol, ethanol, 2-methylpropanol, octadecanol, eicosanol, ethylene glycol, diethylene glycol, tetraethylene glycol, diethylene glycol monoethylether, propylene glycol, tripropylene glycol, glycerol, sorbitol, 1,1,1-trimethylol ethane, 1,1,1-trimethylol propane, 1,1,1-trimethylol butane, pentaerythritol, dipentaerythritol, and the like.

The succinic esters are readily made by merely heating a mixture of alkenyl succinic acid, anhydrides or lower alkyl (e.g., C1-C4) ester with the alcohol while distilling out water or lower alkanol. In the case of acid-esters less alcohol is used. In fact, acid-esters made from alkenyl succinic anhydrides do not evolve water. In another method the alkenyl succinic acid or anhydrides can be merely reacted with an appropriate alkylene oxide such as ethylene oxide, propylene oxide, and the like, including mixtures thereof.

Still another sub-category of carboxylic dispersants useful in forming component b) comprises an alkenyl succinic ester-amide mixture. These may be made by heating the above-described alkenyl succinic acids, anhydrides or lower alkyl esters or etc. with an alcohol and an amine either sequentially or in a mixture. The alcohols and amines described above are also useful in this embodiment. Alternatively, amino alcohols can be used alone or with the alcohol and/or amine to form the ester-amide mixtures. The amino alcohol can contain 1-20 carbon atoms, 1-6 hydroxy groups and 1-4 amine nitrogen atoms. Examples are ethanolamine, diethanolamine, N-ethanol-diethylene triamine, and trimethylol aminomethane.

Here again, the alkenyl group of the succinic ester-amide can be hydrogenated or subjected to other reactions involving olefinic double bonds.

Representative examples of suitable ester-amide mixtures are described in U.S. Pat. Nos. 3,184,474; 3,576,743; 3,632,511; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,991,098; 4,071,548; and 4,173,540.

Yet another sub-category of carboxylic dispersants useful in forming component b) comprises the Mannich-based derivatives of hydroxyaryl succinimides. Such compounds can be made by reacting a polyalkenyl succinic anhydride with an aminophenol to produce an N-(hydroxyaryl) hydrocarbyl

succinimide which is then reacted with an alkylene diamine or polyalkylene polyamine and an aldehyde (e.g., formaldehyde), in a Mannich-base reaction. Details of such synthesis are set forth in U.S. Pat. No. 4,354,950. As in the case of the other carboxylic dispersants discussed above, the alkenyl succinic anhydride or like acylating agent is derived from a polyolefin, preferably a polyisobutene, having a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400, and especially 800 to 1,200. Likewise, residual unsaturation in the polyalkenyl substituent group can be used as a reaction site as for example, by hydrogenation, sulfurization, or the like.

#### Type B - Hydrocarbyl Polyamine Dispersants.

This category of ashless dispersants which can be used in forming component b) is likewise well known to those skilled in the art and fully described in the literature. The hydrocarbyl polyamine dispersants are generally produced by reacting an aliphatic or alicyclic halide (or mixture thereof) containing an average of at least about 40 carbon atoms with one or more amines, preferably polyalkylene polyamines. Examples of such hydrocarbyl polyamine dispersants are described in U.S. Pat. Nos. 3,275,554; 3,438,757; 3,454,555; 3,565,804; 3,671,511; 3,821,302; 3,394,576; and in European Patent Publication No. 382,405.

In general, the hydrocarbyl-substituted polyamines are high molecular weight hydrocarbyl-N-substituted polyamines containing basic nitrogen in the molecule. The hydrocarbyl group typically has a number average molecular weight in the range of about 750-10,000, more usually in the range of about 1,000-5,000.

The hydrocarbyl radical may be aliphatic or alicyclic and, except for adventitious amounts of aromatic components in petroleum mineral oils, will be free of aromatic unsaturation. The hydrocarbyl groups will normally be branched-chain aliphatic, having 0-2 sites of unsaturation, and preferably from 0-1 site of ethylene unsaturation. The hydrocarbyl groups are preferably derived from petroleum mineral oil, or polyolefins, either homo-polymers or higher-order polymers, or 1-olefins of from 2-6 carbon atoms. Ethylene is preferably copolymerized with a higher olefin to insure oil solubility.

Illustrative polymers include polypropylene, polyisobutylene, poly-1-butene, etc. The polyolefin group will normally have at least one branch per six carbon atoms along the chain, preferably at least one branch per four carbon atoms along the chain. These branched-chain hydrocarbons are readily prepared by the polymerization of olefins of from 3-6 carbon atoms and preferably from olefins of from 3-4 carbon atoms.

In preparing the hydrocarbyl polyamine dispersants, rarely will a single compound having a defined structure be employed. With both polymers and petroleum-derived hydrocarbon groups, the composition is a mixture of materials having various structures and molecular weights. Therefore, in referring to molecular weight, number average molecular weights are intended. Furthermore, when speaking of a particular hydrocarbon group, it is intended that the group include the mixture that is normally contained within materials which are commercially available. For example, polyisobutylene is known to have a range of molecular weights and may include small amounts of very high molecular weight materials.

Particularly preferred hydrocarbyl-substituted amines or polyamines are prepared from polyisobutetyl chloride.

The polyamine employed to prepare the hydrocarbyl-substituted polyamine is preferably a polyamine having from 2 to about 12 amine nitrogen atoms and from 2 to about 40 carbon atoms. The polyamine is reacted with a hydrocarbyl halide (e.g., chloride) to produce the hydrocarbyl-substituted polyamine. The polyamine preferably has a carbon-to-nitrogen ratio of from about 1:1 to about 10:1.

The amine portion of the hydrocarbyl-substituted amine may be substituted with substituents selected from (A) hydrogen, and (B) hydrocarbyl groups of from about 1 to about 10 carbon atoms.

The polyamine portion of the hydrocarbyl-substituted polyamine may be substituted with substituents selected from (A) hydrogen, (B) hydrocarbyl groups of from 1 to about 10 carbon atoms, (C) acyl groups of from 2 to about 10 carbon atoms, and (D) monoketo, monohydroxy, mononitro, monocyno, lower alkyl and lower alkoxy derivatives of (B) and (C). "Lower" as used in terms like lower alkyl or lower alkoxy, means a group containing from 1 to about 6 carbon atoms.

At least one of the nitrogens in the hydrocarbyl-substituted amine or polyamine is a basic nitrogen atom, i.e., one titratable by a strong acid.

Hydrocarbyl, as used in describing the substituents in the amine or polyamine used in forming the dispersants, denotes an organic radical composed of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., aralkyl. Preferably, the hydrocarbyl group will be relatively

free of aliphatic unsaturation, i.e., ethylenic and acetylenic, particularly acetylenic unsaturation. The hydrocarbyl substituted polyamines used in forming the dispersants are generally, but not necessarily, N-substituted polyamines. Exemplary hydrocarbyl groups and substituted hydrocarbyl groups which may be present in the amine portion of the dispersant include alkyls such as methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl, octyl, etc., alkenyls such as propenyl, isobutenyl, hexenyl, octenyl, etc., hydroxyalkyls, such as 2-hydroxyethyl, 3-hydroxypropyl, hydroxyisopropyl, 4-hydroxybutyl, etc., ketoalkyls, such as 2-ketopropyl, 6-ketoctyl, etc., alkoxy and lower alenoxy alkyls, such as ethoxyethyl, ethoxypropyl, propoxyethyl, propoxypropyl, 2-(2-ethoxyethoxy)ethyl, 2-(2-(2-ethoxyethoxy)ethoxy)ethyl, 3,6,9,12-tetraoxytetradecyl, 2-(2-ethoxyethoxy)hexyl, etc.

Typical amines useful in preparing the hydrocarbyl-substituted amines include methylamine, dimethylamine, ethylamine, diethylamine, n-propylamine, di-n-propylamine, etc. Such amines are either commercially available or are prepared by art recognized procedures.

The polyamine component may also contain heterocyclic polyamines, heterocyclic substituted amines and substituted heterocyclic compounds, wherein the heterocyclic comprises one or more 5-6 membered rings containing oxygen and/or nitrogen. Such heterocyclics may be saturated or unsaturated and substituted with groups selected from the aforementioned (A), (B), (C), and (D). The heterocyclics are exemplified by piperazines, such as 2-methylpiperazine, 1,2-bis(N-piperazinyl-ethane), and N,N min -bis(N-piperazinyl)piperazine, 2-methylimidazoline, 3-aminopiperidine, 2-aminopyridine, 2-( beta -aminoethyl)-3-pyrrolidine, 3-aminopyrrolidine, N-(3-aminopropyl)morpholine, etc. Among the heterocyclic compounds, the piperazines are preferred.

Typical polyamines that can be used to form the hydrocarbyl polyamine dispersants include the following: ethylene diamine, 1,2-propylene diamine, 1,3-propylene diamine, diethylene triamine, triethylene tetramine, hexamethylene diamine, tetraethylene pentamine, methylaminopropylene diamine, N-( beta -aminoethyl)piperazine, N,N min -di( beta -aminoethyl)piperazine, N,N min -di( beta -aminoethyl)imidazolidone-2, N-( beta -cyanoethyl)ethane-1,2-diamine, 1,3,6,9-tetraaminooctadecane, 1,3,6-triamino-9-oxadecane, N-methyl-1,2-propanediamine, 2-(2-aminoethylamino)-ethanol, and the like.

Another group of suitable polyamines are the polyalkylene amines in which the alkylene groups differ in carbon content, such as for example bis(aminopropyl)ethylenediamine. Such compounds are prepared by the reaction of acrylonitrile with an ethylenamine, for example, an ethylenamine having the formula H<sub>2</sub>H(CH<sub>2</sub>CH<sub>2</sub>NH)<sub>n</sub>H wherein n is an integer from 1 to 5, followed by hydrogenation of the resultant intermediate. Thus, the product prepared from ethylene diamine and acrylonitrile has the formula H<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>.

In many instances the polyamine used as a reactant in the production of the hydrocarbyl-substituted polyamine is not a single compound but a mixture in which one or several compounds predominate with the average composition indicated. For example, tetraethylene pentamine prepared by the polymerization of aziridine or the reaction of 1,2-dichloroethane and ammonia will have both lower and higher amine members, e.g., triethylene tetramine, substituted piperazines and pentaethylene hexamine, but the composition will be largely tetraethylene pentamine and the empirical formula of the total amine composition will closely approximate that of tetraethylene pentamine. Finally, in preparing the hydrocarbyl-substituted polyamines for use in this invention, where the various nitrogen atoms of the polyamine are not geometrically equivalent, several substitutional isomers are possible and are encompassed with the final product. Methods of preparation of polyamines and their reactions are detailed in Sidgewick, The Organic Chemistry of Nitrogen, Clarendon Press, Oxford, 1966; Nollier, Chemistry of Organic Compounds, Saunders, Philadelphia, 2nd Ed., 1957; and Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, especially volume 2, pp. 99-116.

The preferred hydrocarbyl-substituted polyalkylene polyamines for use in this invention may be represented by the formula R<sub>1</sub>NH-(R<sub>2</sub>-NH-)<sub>alpha</sub>-H wherein R<sub>1</sub> is hydrocarbyl having an average molecular weight of from about 750 to about 10,000; R<sub>2</sub> is alkylene of from 2 to 6 carbon atoms; and alpha is an integer of from 0 to about 10.

Preferably, R<sub>1</sub> is hydrocarbyl having an average molecular weight of from about 1,000 to about 10,000. Preferably, R<sub>2</sub> is alkylene of from 2 to 3 carbon atoms and alpha is preferably an integer of from 1 to 6.

#### Type C - Mannich polyamine dispersants.

This category of ashless dispersant which can be utilized in the formation of component b) is comprised of reaction products of an alkyl phenol, with one or more aliphatic aldehydes containing from 1 to about 7 carbon atoms (especially formaldehyde and derivatives thereof), and polyamines (especially polyalkylene polyamines of the type described hereinabove). Examples of these Mannich polyamine dispersants are

described in the following U.S. Patents: 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,558,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,980,569; and 4,011,380.

The polyamine group of the Mannich polyamine dispersants is derived from polyamine compounds characterized by containing a group of the structure -NH- wherein the two remaining valances of the nitrogen are satisfied by hydrogen, amino, or organic radicals bonded to said nitrogen atom. These compounds include aliphatic, aromatic, heterocyclic and carbocyclic polyamines. The source of the oil-soluble hydrocarbyl group in the Mannich polyamine dispersant is a hydrocarbyl-substituted hydroxy aromatic compound comprising the reaction product of a hydroxy aromatic compound, according to well known procedures, with a hydrocarbyl donating agent or hydrocarbon source. The hydrocarbyl substituent provides substantial oil solubility to the hydroxy aromatic compound and, preferably, is substantially aliphatic in character. Commonly, the hydrocarbyl substituent is derived from a polyolefin having at least about 40 carbon atoms. The hydrocarbon source should be substantially free from pendant groups which render the hydrocarbyl group oil insoluble. Examples of acceptable substituent groups are halide, hydroxy, ether, carboxy, ester, amide, nitro and cyano. However, these substituent groups preferably comprise no more than about 10 weight percent of the hydrocarbon source.

The preferred hydrocarbon sources for preparation of the Mannich polyamine dispersants are those derived from substantially saturated petroleum fractions and olefin polymers, preferably polymers of mono-olefins having from 2 to about 30 carbon atoms. The hydrocarbon source can be derived, for example, from polymers of olefins such as ethylene, propene, 1-butene, isobutene, 1-octene, 1-methylcyclohexene, 2-butene and 3-pentene. Also useful are copolymers of such olefins with other polymerizable olefinic substances such as styrene. In general, these copolymers should contain at least 80 percent and preferably about 95 percent, on a weight basis, of units derived from the aliphatic mono-olefins to preserve oil solubility. The hydrocarbon source generally contains at least about 40 and preferably at least about 50 carbon atoms to provide substantial oil solubility to the dispersant. The olefin polymers having a number average molecular weight between about 600 and 5,000 are preferred for reasons of easy reactivity and low cost. However, polymers of higher molecular weight can also be used. Especially suitable hydrocarbon sources are isobutylene polymers.

The Mannich polyamine dispersants are generally prepared by reacting a hydrocarbyl-substituted hydroxy aromatic compound with an aldehyde and a polyamine. Typically, the substituted hydroxy aromatic compound is contacted with from about 0.1 to about 10 moles of polyamine and about 0.1 to about 10 moles of aldehyde per mole of substituted hydroxy aromatic compound. The reactants are mixed and heated to a temperature above about 80 DEG C. to initiate the reaction. Preferably, the reaction is carried out at a temperature from about 100 DEG to about 250 DEG C. The resulting Mannich product has a predominantly benzylamine linkage between the aromatic compound and the polyamine. The reaction can be carried out in an inert diluent such as mineral oil, benzene, toluene, naphtha, ligroin, or other inert solvents to facilitate control of viscosity, temperature and reaction rate.

Polyamines are preferred for use in preparing the Mannich polyamine dispersants, and suitable polyamines include, but are not limited to, alkylene diamines and polyalkylene polyamines (and mixtures thereof) of the formula: EMI36.1 wherein n is an integer from 1 to about 10, R is a divalent hydrocarbyl group of from 1 to about 18 carbon atoms, and each A is independently selected from the group consisting of hydrogen and monovalent aliphatic groups containing up to 10 carbon atoms which can be substituted with one or two hydroxyl groups. Most preferably, R is a lower alkylene group of from 2 to 6 carbon atoms and A is hydrogen.

Suitable polyamines for use in preparation of the Mannich polyamine dispersants include, but are not limited to, methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines and heptylene polyamines. The higher homologs of such amines and related aminoalkyl-substituted piperazines are also included. Specific examples of such polyamines include ethylene diamine, triethylene tetramine, tris(2-aminoethyl)-amine, propylene diamine, pentamethylene diamine, hexamethylene diamine, heptamethylene diamine, octamethylene diamine, decamethylene diamine, di(heptamethylene) triamine, pentaethylene hexamine, di(trimethylene) triamine, 2-heptyl-3-(2-aminopropyl)imidazoline, 1,3-bis(2-aminoethyl)imidazoline, 1-(2-aminopropyl)piperazine, 1,4-bis(2-aminoethyl)piperazine and 2-methyl-1-(2-aminobutyl)piperazine. Higher homologs, obtained by condensing two or more of the above mentioned amines, are also useful, as are the polyoxyalkylene polyamines.

The polyalkylene polyamines, examples of which are set forth above, are especially useful in preparing the Mannich polyamine dispersants for reasons of cost and effectiveness. Such polyamines are described in detail under the heading "Diamines and Higher Amines" in Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Vol. 7, pp. 22-39. They are prepared most conveniently by the reaction of an

ethylene imine with a ring-opening reagent such as ammonia. These reactions result in the production of somewhat complex mixtures of polyalkylene polyamines which include cyclic condensation products such as piperazines. Because of their availability, these mixtures are particularly useful in preparing the Mannich polyamine dispersants. However, it will be appreciated that satisfactory dispersants can also be obtained by use of pure polyalkylene polyamines.

Alkylene diamines and polyalkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atom are also useful in preparing the Mannich polyamine dispersants. These materials are typically obtained by reaction of the corresponding polyamine with an epoxide such as ethylene oxide or propylene oxide. Preferred hydroxyalkyl-substituted diamines and polyamines are those in which the hydroxyalkyl groups have less than about 10 carbon atoms. Examples of suitable hydroxyalkyl-substituted diamines and polyamines include, but are not limited to, N-(2-hydroxyethyl)ethylenediamine, N,N min -bis (2-hydroxyethyl)ethylenediamine, mono(hydroxypropyl)diethylenetriamine, (di(hydroxypropyl)tetraethylenepentamine and N-(3-hydroxybutyl)tetramethylenediamine. Higher homologs obtained by condensation of the above mentioned hydroxyalkyl-substituted diamines and polyamines through amine groups or through ether groups are also useful.

Any conventional formaldehyde yielding reagent is useful for the preparation of the Mannich polyamine dispersants. Examples of such formaldehyde yielding reagents are trioxane, paraformaldehyde, trioxymethylene, aqueous formalin and gaseous formaldehyde.

#### Type D - Polymeric polyamine dispersants.

Also suitable for preparing component b) of the compositions of this invention are polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such polymeric dispersants are herein referred to as polymeric polyamine dispersants. Such materials include, but are not limited to, interpolymers of decyl methacrylate, vinyl decyl ether or a relatively high molecular weight olefin with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in the following patents: U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; 3,702,300.

#### Type E - Post-treated basic nitrogen-containing and/or hydroxyl-containing ashless dispersants.

As is well known in the art, any of the ashless dispersants referred to above as types A-D can be subjected to post-treatment with one or more suitable reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, anhydrides of low molecular weight dibasic acids, nitriles, epoxides, and the like. Such post-treated ashless dispersants can be used in forming component b) of the compositions of this invention provided that the post-treated dispersant contains residual basic nitrogen and/or one or more residual hydroxyl groups. Alternatively, the phosphorylated and boronated dispersant can be subjected to post-treatment with such reagents. Likewise, the post-treatment can be conducted in between the phosphorylation and boronation or conversely, between the boronation and the phosphorylation. Examples of post-treatment procedures and post-treated ashless dispersants are set forth in the following U.S. Patents: 3,036,003; 3,087,936; 3,200,107; 3,216,936; 3,254,025; 3,256,185; 3,278,550; 3,218,428; 3,280,234; 3,281,428; 3,282,955; 3,312,619; 3,366,569; 3,367,943; 3,373,111; 3,403,102; 3,442,808; 3,455,831; 3,455,832; 3,493,520; 3,502,677; 3,513,093; 3,533,945; 3,539,633; 3,573,010; 3,579,450; 3,591,598; 3,600,372; 3,639,242; 3,649,229; 3,649,659; 3,658,836; 3,697,574; 3,702,757; 3,703,536; 3,704,308; 3,708,422; 4,025,445; and 4,857,214.

Mannich-based derivatives of hydroxyaryl succinimides that have been post-treated with C5-C9 lactones such as epsilon -caprolactone and optionally with other post-treating agents as described for example in U.S. Pat. No. 4,971,711 can also be utilized in forming component b) for use in the practice of this invention, provided that such post-treated Mannich-based derivatives of hydroxyaryl succinimides contain basic nitrogen, and/or at least one hydroxyl group. The disclosures of U.S. Pat. No. 4,971,711, as well as related U.S. Pat. Nos. 4,820,432; 4,828,742; 4,866,135; 4,866,139; 4,866,140; 4,866,141; 4,866,142; 4,906,394; and 4,913,830 are referred to as regards additional suitable basic nitrogen-containing and/or hydroxyl group-containing ashless dispersants which may be utilized in forming component b).

One preferred category of post-treated ashless dispersants is comprised of basic nitrogen-containing and/or hydroxyl group-containing ashless dispersants which have been heated with (1) a phosphorus compound such that they contain phosphorus, or (2) a boron compound such that they contain boron, all with the proviso that such post-treated products contain residual basic nitrogen and/or one or more residual hydroxyl groups. Numerous examples of such dispersants and methods for their production are described in the U.S. Patents referred to at the outset of this disclosure under the caption "Background".

The boron-containing post-treated ashless dispersants of the prior art type can be converted into a material suitable for use as component b) simply by conducting a phosphorylation in the manner described herein. If desired, additional boron can also be incorporated into a prior art type post-treated boron-containing ashless dispersant by conducting a boronation in the manner described herein either before, during or after the phosphorylation. Likewise, the phosphorus-containing post-treated ashless dispersants of the prior art type can be converted into a material suitable for use as component b) simply by conducting a boronation in the manner described herein. If desired, additional phosphorus can also be incorporated into a prior art type post-treated phosphorus-containing ashless dispersant by conducting a phosphorylation in the manner described herein either before, during or after the boronation. It is also possible by using the phosphorylation and/or boronation procedures described herein to phosphorylate and/or boronate a post-treated ashless dispersant that already contains both phosphorus and boron, again provided that such initial post-treated ashless dispersant contains at least some residual basic nitrogen and/or at least some residual hydroxyl substitution.

The ashless dispersant(s) used in forming component b) can be any mixture containing any two or more ashless dispersants containing basic nitrogen and/or at least one hydroxyl group. Thus, for example, with reference to dispersants of the above types A, B, C, D and E, use can be made of such mixtures as:

- (1) Two or more different type A dispersants;
- (2) Two or more different type B dispersants;
- (3) Two or more different type C dispersants;
- (4) Two or more different type D dispersants;
- (5) Two or more different type E dispersants;
- (6) One or more type A dispersants with one or more type B dispersants;
- (7) One or more type A dispersants with one or more type C dispersants;
- (8) One or more type A dispersants with one or more type D dispersants;
- (9) One or more type A dispersants with one or more type E dispersants;
- (10) One or more type B dispersants with one or more type C dispersants;
- (11) One or more type B dispersants with one or more type D dispersants;
- (12) One or more type B dispersants with one or more type E dispersants;
- (13) One or more type C dispersants with one or more type D dispersants;
- (14) One or more type C dispersants with one or more type E dispersants;
- (15) One or more type D dispersants with one or more type E dispersants;
- (16) One or more type A dispersants with one or more type B dispersants and with one or more type C dispersants;
- (17) One or more type A dispersants with one or more type B dispersants and with one or more type D dispersants;
- (18) One or more type A dispersants with one or more type B dispersants and with one or more type E dispersants;
- (19) One or more type A dispersants with one or more type C dispersants and with one or more type D dispersants;
- (20) One or more type A dispersants with one or more type C dispersants and with one or more type E dispersants;
- (21) One or more type A dispersants with one or more type D dispersants and with one or more type E dispersants;
- (22) One or more type B dispersants with one or more type C dispersants and with one or more type D dispersants;
- (23) One or more type B dispersants with one or more type C dispersants and with one or more type E dispersants;
- (24) One or more type B dispersants with one or more type D dispersants and with one or more type E dispersants;
- (25) One or more type C dispersants with one or more type D dispersants and with one or more type E dispersants;
- (26) One or more type A dispersants with one or more type B dispersants, with one or more type C dispersants, and with one or more type D dispersants;
- (27) One or more type A dispersants with one or more type B dispersants, with one or more type C dispersants, and with one or more type E dispersants;
- (28) One or more type A dispersants with one or more type C dispersants, with one or more type D dispersants, and with one or more type E dispersants;
- (29) One or more type B dispersants with one or more type C dispersants, with one or more type D dispersants, and with one or more type E dispersants; and
- (30) One or more type A dispersants with one or more type B dispersants, with one or more type C dispersants, with one or more type D dispersants, and with one or more type E dispersants.

It will also be understood that any given type of dispersant whether used with one or more other dispersant types or without any other dispersant type can comprise:

- (I) A mixture in which at least one component contains basic nitrogen but no hydroxyl group and another component of the mixture contains at least one hydroxyl group but no basic nitrogen;

- (II) A mixture in which at least one component contains basic nitrogen but no hydroxyl group and another component of the mixture contains basic nitrogen and at least one hydroxyl group;
- (III) A mixture in which at least one component contains at least one hydroxyl group but no basic nitrogen and another component of the mixture contains basic nitrogen and at least one hydroxyl group; and
- (IV) A mixture in which at least one component contains basic nitrogen but no hydroxyl group, another component of the mixture contains at least one hydroxyl group but no basic nitrogen, and still another component of the mixture contains basic nitrogen and at least one hydroxyl group.

Because of environmental and conservational concerns it is desirable to employ ashless dispersants which contain little, if any, halogen atoms such as chlorine atoms. Thus, in order to satisfy such concerns, it is desirable (although not necessary from a performance standpoint) to select ashless dispersants (as well as the other components used in the compositions of this invention) such that the total halogen content, if any, of the overall lubricant or functional fluid composition does not exceed 100 ppm. Indeed, the lower the better. Likewise, it is preferable in accordance with this invention, to provide additive concentrates which, when dissolved in a halogen-free base oil, at a concentration of 10% by weight, yield an oleaginous composition in which the total halogen content, if any, is 100 ppm or less.

Suitable compounds of boron useful in forming the phosphorylated and boronated ashless dispersants for use as component b) include, for example, boron acids, boron oxides, boron esters, and amine or ammonium salts of boron acids. Illustrative compounds include boric acid (sometimes referred to as orthoboric acid), boronic acid, tetraboric acid, metaboric acid, pyroboric acid, esters of such acids, such as mono-, di-, and tri-organic esters with alcohols or polyols having up to 20 or more carbon atoms (e.g., methanol, ethanol, 2-propanol, propanol, butanols, pentanols, hexanols, ethylene glycol, propylene glycol, trimethylol propane, diethanol amine, etc.), boron oxides such as boric oxide and boron oxide hydrate, and ammonium salts such as ammonium borate, ammonium pyroborate, etc. While usable, boron halides such as boron trifluoride, boron trichloride, and the like, are undesirable as they tend to introduce halogen atoms into the boronated dispersant, a feature which is detrimental from the environmental, toxicological and conservational standpoints. Amine borane addition compounds and hydrocarbyl boranes can also be used, although they tend to be relatively expensive. The preferred boron reagent is boric acid, H<sub>3</sub>BO<sub>3</sub>.

For further details concerning procedures for conducting the boronation operation apart from the phosphorylation operation, reference may be had, for example, to the disclosures of U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 3,284,410; 3,338,832; 3,344,069; 3,533,945; 3,718,663; 4,097,389; 4,554,086; and 4,634,543.

#### Producing Phosphorylated and Boronated Ashless Dispersants from at least one Inorganic Phosphorus Compound and at least one Boron Compound

Typical procedures for producing the phosphorylated and boronated ashless dispersants from (i) and (iii) above involve concurrently or sequentially heating one or more ashless dispersants of the types described above with at least one inorganic phosphorus compound and at least one boron compound under conditions yielding a liquid phosphorus- and boron-containing composition. Examples of inorganic phosphorus compounds which are useful in forming such products include phosphorous acid (H<sub>3</sub>PO<sub>3</sub>, sometimes depicted as H<sub>2</sub>(HPO<sub>3</sub>), and sometimes called ortho-phosphorous acid or phosphonic acid), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, sometimes called orthophosphoric acid), hypophosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>6</sub>), metaphosphoric acid (HPO<sub>3</sub>), pyrophosphoric acid (H<sub>4</sub>P<sub>2</sub>O<sub>7</sub>), hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>, sometimes called phosphinic acid), pyrophosphorous acid (H<sub>4</sub>P<sub>2</sub>O<sub>5</sub>, sometimes called pyrophosphonic acid), phosphinous acid (H<sub>3</sub>PO), tripolyphosphoric acid (H<sub>5</sub>P<sub>3</sub>O<sub>10</sub>), tetrapolyphosphoric acid (H<sub>6</sub>P<sub>4</sub>O<sub>13</sub>), trimetaphosphoric acid (H<sub>3</sub>P<sub>3</sub>O<sub>9</sub>), phosphorus trioxide, phosphorus tetraoxide, phosphorus pentoxide, and the like. Partial or total sulfur analogs such as phosphorotetrathioic acid (H<sub>3</sub>PS<sub>4</sub>), phosphoromonothioic acid (H<sub>3</sub>PO<sub>3</sub>S), phosphorodithioic acid (H<sub>3</sub>PO<sub>2</sub>S<sub>2</sub>), phosphorotrithioic acid (H<sub>3</sub>POS<sub>3</sub>), phosphorus sesquisulfide, phosphorus heptasulfide, and phosphorus pentasulfide (P<sub>2</sub>S<sub>5</sub>, sometimes referred to as P<sub>4</sub>S<sub>10</sub>) can also be used in forming products suitable for use as component b) in the practice of this invention. Also usable, though less preferred, are the inorganic phosphorus halide compounds such as PCI<sub>3</sub>, PBr<sub>3</sub>, POCl<sub>3</sub>, PSCl<sub>3</sub>, etc. The preferred phosphorus reagent is phosphorous acid, (H<sub>3</sub>PO<sub>3</sub>).

It will be understood and appreciated by those skilled in the art that the form or composition of the inorganic compound(s) as charged into the mixture to be heated or being heated may be altered in situ. For example, the action of heat and/or water can transform certain inorganic phosphorus compounds into other inorganic phosphorus compounds or species. Any such in situ transformations that may occur are within the purview of this invention provided that the liquid phosphorylated ashless dispersant reveals on analysis the presence therein of phosphorus (as well as boron).

Optionally, additional sources of basic nitrogen can be included in the inorganic phosphorus compound-

ashless dispersant-boron compound mixture so as to provide a molar amount (atomic proportion) of basic nitrogen up to that equal to the molar amount of basic nitrogen contributed by the ashless dispersant. Preferred auxiliary nitrogen compounds are long chain primary, secondary and tertiary alkyl amines containing from about 12 to 24 carbon atoms, including their hydroxyalkyl and aminoalkyl derivatives. The long chain alkyl group may optionally contain one or more ether groups. Examples of suitable compounds are oleyl amine, N-oleyltrimethylene diamine, N-tallow diethanolamine, N,N-dimethyl oleylamine, and myristyloxapropyl amine.

Other materials normally used in lubricant additives which do not interfere with the process may also be added, for example, a benzotriazole, including lower (C1-C4) alkyl-substituted benzotriazoles, which function to protect copper surfaces.

The concurrent heating step or the combination of sequential heating steps is conducted at temperatures sufficient to produce a final liquid composition which contains both phosphorus and boron. The heating can be carried out in the absence of a solvent by heating a mixture of the ashless dispersant and one or more suitable inorganic phosphorus compounds, or one or more suitable boron compounds, or, preferably, a combination of one or more suitable inorganic phosphorus compounds and one or more suitable boron compounds. The temperatures used will vary somewhat depending upon the nature of the ashless dispersant and the inorganic phosphorus and/or boron reagent being utilized. Generally speaking however, the temperature will usually fall within the range of about 40 to about 200 DEG C. The duration of the heating is likewise susceptible to variation, but ordinarily will fall in the range of about 1 to about 3 hours. When conducting the heating in bulk, it is important to thoroughly agitate the components to insure intimate contact therebetween. When utilizing the preferred phosphorus and boron reagents (phosphorous acid and boric acid), it is preferable to add water to facilitate initial dissolution of the boric acid. Alternatively, the phosphorous acid may be utilized in the form of an aqueous solution thereby introducing water into the system to facilitate dissolution of the boric acid. Water (and when using boron esters, alcohol) formed in the process and any added water is preferably removed from the heated mixture by vacuum distillation at temperatures of from about 100 to about 140 DEG C. Preferably the heating step or steps will be conducted in a diluent oil or other inert liquid medium such as light mineral oils, and the like.

The amount of phosphorus compound employed in the heating process ranges from about 0.001 mole to 0.999 mole per mole of basic nitrogen and free hydroxyl in the mixture being heated, up to one half of which may be contributed by an auxiliary nitrogen compound. The amount of boron compound employed ranges from about 0.001 mole to about 1 mole per mole of basic nitrogen and/or hydroxyl in the mixture which is in excess of the molar amount of inorganic phosphorus compound. When conducting the phosphorylation and boronation on a sequential basis (or when conducting one of these operations on a dispersant which has previously been subjected to the other such operation), the last-to-be-used reagent(s) – inorganic phosphorus compound(s) or boron compound(s), as the case may be – can be used in an amount equivalent to (or even in excess of) the amount of basic nitrogen and/or hydroxyl groups in the dispersant being heated with such last-to-be-used reagent(s).

When used, the amount of added water is not particularly critical as it is removed by distillation during the course of, or at the end of, the heating step. Amounts of up to 1% by weight of the mixture being heated are preferred. When used, the amount of diluent usually ranges from about 10 to about 50% by weight of the mixture being subjected to heating.

When conducting the preferred concurrent heating step for production of component b), it is desirable to employ procedures such as described in U.S. Pat. No. 4,857,214.

When forming component b) in part by use of one or more organic phosphorus compounds such as one or more organic phosphates (e.g., trihydrocarbyl phosphates, dihydrocarbyl monoacid phosphates, monohydrocarbyl diacid phosphates, or mixtures thereof), phosphites (e.g., trihydrocarbyl phosphites, dihydrocarbyl hydrogen phosphites, hydrocarbyl diacid phosphites, or mixtures thereof), phosphonates (e.g., hydrocarbyl phosphonic acids, mono- and/or dihydrocarbyl esters of phosphonic acids, or mixtures thereof), phosphonites (e.g., hydrocarbyl phosphinic acids, mono- and/or dihydrocarbyl esters of phosphinic acids, or mixtures thereof), etc., or the partial or total sulfur analogs thereof, and in part by use of one or more inorganic phosphorus compounds, the latter should be used in an amount sufficient to provide at least 10% (preferably at least 50% and more preferably at least 75%) of the total content of phosphorus in the phosphorylated and boronated dispersant. For crankcase lubricant usage, component b) when in the undiluted state preferably contains at least 3,000 ppm (more preferably at least 5,000 ppm and most preferably at least 7,000 ppm) of phosphorus and at least 1,500 ppm (more preferably at least 2,500 ppm and most preferably at least 3,500 ppm) of boron.

The preparation from (i) and (iii) of phosphorylated and boronated ashless dispersants suitable for use as component b) in the compositions of this invention is illustrated by the following examples in which all parts and percentages are by weight unless otherwise clearly specified.

### EXAMPLE A-1

A mixture is formed from 260 parts of a commercial succinimide ashless dispersant (HiTEC TM 644 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.), 100 parts of a 100 Solvent Neutral refined mineral oil diluent, 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

### EXAMPLE A-2

The procedure of Example A-1 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 1,100. The average number of succinic groups per alkenyl group in the succinimide is approximately 1.2.

### EXAMPLE A-3

The procedure of Example A-1 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 2,100.

### EXAMPLE A-4

The procedure of Example A-1 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a Mannich polyamine dispersant (AMOCO TM 9250 dispersant; Amoco Corporation). The Amoco 9250 dispersant as supplied by the manufacturer is believed to be a boronated dispersant and in such case, another material suitable for use as component b) can be formed by eliminating the boric acid and water from the procedure used in this example and thereby conducting phosphorylation on an already boronated dispersant.

### EXAMPLE A-5

The procedure of Example A-1 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a commercial ashless dispersant of the pentaerythritol succinic ester type (Lubrizol TM 936 dispersant; The Lubrizol Corporation). As in the case of Example A-4, the initial dispersant as supplied by the manufacturer is believed to be a boronated dispersant. In such cases, the dispersant can, if desired, be subjected just to phosphorylation to thereby form still another product suitable for use as component b).

### EXAMPLE A-6

The procedure of Example A-1 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P2S5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100 DEG C to provide a clear, oil-soluble composition suitable for use as component b).

### EXAMPLE A-7

The procedure of Example A-6 is repeated except that the P2S5 is replaced by 7 parts of phosphorus pentoxide (P2O5).

### EXAMPLE A-8

The procedures of Examples A-1 through A-7 are repeated except that the tolutriazole is omitted from the initial mixtures subjected to the thermal processes.

#### EXAMPLE A-9

A mixture of 11,904 parts of a commercial boronated succinimide (HiTEC TM 648 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.) and 96 parts of phosphorous acid is heated to 100-110 DEG C for 2 hours to form a homogeneous liquid composition suitable for use as component b) in the practice of this invention. For convenience in handling, 100 Solvent Neutral mineral oil can be added to form an 80% solution of the additive in the oil.

#### EXAMPLE A-10

A mixture of 260 parts of a commercial succinimide (HiTEC TM 644 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.), and 8 parts of phosphorous acid is heated to 100 DEG C for 2 hours. To this product is added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100 DEG C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE A-11

A mixture of 260 parts of a commercial succinimide (HiTEC TM 644 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.), 8 parts of orthoboric acid and 4 parts of water is heated to 100 DEG C for 2 hours. Then 8 parts of phosphorous acid is added to the reaction mixture and the temperature of the mixture is held at 100 DEG C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE A-12

A mixture of 260 parts of a commercial succinic pentaerythritol ester ashless dispersant (Lubrizol TM 936 dispersant; The Lubrizol Corporation), and 8 parts of phosphorous acid is heated to 100 DEG C for 2 hours. To this product is added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100 DEG C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE A-13

A mixture of 260 parts of a commercial succinic pentaerythritol ester ashless dispersant (Lubrizol TM 936 dispersant; The Lubrizol Corporation), 8 parts of orthoboric acid and 4 parts of water is heated to 100 DEG C for 2 hours. Then 8 parts of phosphorous acid is added to the reaction mixture and the temperature of the mixture is held at 100 DEG C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE A-14

A mixture of 260 parts of a commercial Mannich polyamine dispersant (AMOCO TM 9250 dispersant; Amoco Corporation), and 8 parts of phosphorous acid is heated to 100 DEG C for 2 hours. To this product is added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100 DEG C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of

Hg and gradually raising the temperature to 110 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE A-15

A mixture of 260 parts of a commercial Mannich polyamine dispersant (AMOCO TM 9250 dispersant; Amoco Corporation), 8 parts of orthoboric acid and 4 parts of water is heated to 100 DEG C for 2 hours. Then 8 parts of phosphorus acid is added to the reaction mixture and the temperature of the mixture is held at 100 DEG C for another 2 hours. Water present in the reaction mixture is removed by applying a vacuum of 40 mm of Hg and gradually raising the temperature to 110 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE A-16

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 57 parts (1.38 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 1,067 parts of mineral oil and 893 parts (1.38 equivalents) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140-145 DEG C. The reaction mixture is then heated to 155 DEG C over a three hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominantly of polyisobutyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE A-17

The procedure of Example A-16 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE A-18

The procedure of Example A-16 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P2S5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100 DEG C to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE A-19

The procedure of Example A-18 is repeated except that the P2S5 is replaced by 7 parts of phosphorus pentoxide (P2O5).

#### EXAMPLE A-20

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The

reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutetyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 18.2 parts (0.433 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 392 parts of mineral oil and 348 parts (0.52 equivalent) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140 DEG C. The reaction mixture is then heated to 150 DEG C in 1.8 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominantly of polyisobutetyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutetyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE A-21

The procedure of Example A-20 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE A-22

The procedure of Example A-20 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P2S5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100 DEG C to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE A-23

The procedure of Example A-22 is repeated except that the P2S5 is replaced by 7 parts of phosphorus pentoxide (P2O5).

#### EXAMPLE A-24

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutetyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier (Dow Chemical Company) is heated at 150 DEG C for 2.5 hours. The reaction mixture is then heated to 210 DEG C over a period of 5 hours and then held at 210 DEG C for an additional 3.2 hours. The reaction mixture is cooled to 190 DEG C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205 DEG C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE A-25

The procedure of Example A-24 is repeated except that the tolutriazole is eliminated from the reaction

mixture of (c).

#### EXAMPLE A-26

The procedure of Example A-24 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P2S5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100 DEG C to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE A-27

The procedure of Example A-26 is repeated except that the P2S5 is replaced by 7 parts of phosphorus pentoxide (P2O5).

#### EXAMPLE A-28

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutetyl succinic acylating agent.

(b) A mixture of 3225 parts (5.0 equivalents) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 289 parts (8.5 equivalents) of pentaerythritol and 5204 parts of mineral oil is heated at 225-235 DEG C for 5.5 hours. The reaction mixture is filtered at 130 DEG C to yield an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE A-29

The procedure of Example A-28 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE A-30

The procedure of Example A-28 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P2S5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100 DEG C to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE A-31

The procedure of Example A-30 is repeated except that the P2S5 is replaced by 7 parts of phosphorus pentoxide (P2O5).

#### EXAMPLE A-32

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The

reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutetyl succinic anhydride acylating agent.

(b) A mixture of 322 parts (0.5 equivalent) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 68 parts (2.0 equivalents) of pentaerythritol and 508 parts of mineral oil is heated at 204-227 DEG C for 5 hours. The reaction mixture is cooled to 162 DEG C and 5.3 parts (0.13 equivalent) of a commercial ethylene polyamine mixture having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is heated at 162-163 DEG C for 1 hour, then cooled to 130 DEG C and filtered. The filtrate is an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 350 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE A-33

The procedure of Example A-32 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE A-34

The procedure of Example A-32 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P2S5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100 DEG C to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE A-35

The procedure of Example A-34 is repeated except that the P2S5 is replaced by 7 parts of phosphorus pentoxide (P2O5).

#### EXAMPLE A-36

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ( $M_n = 1845$ ;  $M_w = 5325$ , both as per U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 190 DEG C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192 DEG C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193 DEG C with nitrogen blowing for 10 hours. The residue is predominantly polyisobutetyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier (Dow Chemical Company) is heated at 150 DEG C for 2.5 hours. The reaction mixture is then heated to 210 DEG C over a period of 5 hours and then held at 210 DEG C for an additional 3.2 hours. The reaction mixture is cooled to 190 DEG C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205 DEG C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 260 parts of the ashless dispersant product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE A-37

The procedure of Example A-36 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

### EXAMPLE A-38

The procedure of Example A-36 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P2S5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100 DEG C to provide a clear, oil-soluble composition suitable for use as component b).

### EXAMPLE A-39

The procedure of Example A-38 is repeated except that the P2S5 is replaced by 7 parts of phosphorus pentoxide (P2O5).

### EXAMPLE A-40

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ( $M_n = 1845$ ;  $M_w = 5325$ , both as per U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 190 DEG C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192 DEG C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193 DEG C with nitrogen blowing for 10 hours. The residue is predominantly polyisobutenyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 10.2 parts (0.25 equivalent) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 113 parts of mineral oil and 161 parts (0.25 equivalent) of the substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 138 DEG C. The reaction mixture is heated to 150 DEG C over a 2 hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 125 parts of the polyisobutenyl succinimide product solution formed as in (b), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

### EXAMPLE A-41

The procedure of Example A-40 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

### EXAMPLE A-42

The procedure of Example A-40 is repeated except that 11 parts of phosphorus pentasulfide is used in place of the phosphorous acid, the P2S5 is added to the mixture after water distillation, and the mixture is then heated for an additional hour at 100 DEG C to provide a clear, oil-soluble composition suitable for use as component b).

### EXAMPLE A-43

The procedure of Example A-42 is repeated except that the P2S5 is replaced by 7 parts of phosphorus pentoxide (P2O5).

### EXAMPLE A-44

To a reactor are charged under a nitrogen atmosphere 67.98 parts of a commercially-available

polyisobutetyl succinimide of a mixture of polyethylene polyamines having the approximate overall composition of tetraethylene pentamine (the polyisobutetyl group derived from polyisobutene having a number average molecular weight of about 900; the succinimide product having a ratio of about 1.15 succinic groups per alkenyl group) and 26.14 parts of a 100 Solvent neutral refined mineral oil. After raising the temperature of the resulting solution to 100-105 C, 2.09 parts of boric acid and 2.09 parts of phosphorous acid are introduced into the reactor, followed by 0.92 part of tolutriazole (Cobratec TT-100; PMC Specialties Group, Cincinnati, Ohio) and then 0.78 part of water. The resultant mixture is heated at 100-105 DEG C for two hours and then the temperature is gradually raised to 115 DEG C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120 DEG C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

#### EXAMPLE A-45

The procedure of Example A-44 is repeated except that the tolutriazole is omitted from the reaction mixture.

#### EXAMPLE A-46

(a) A mixture of 322 parts of the polyisobutene-substituted succinic acylating agent prepared as in Example A-40(a), 68 parts of pentaerythritol and 508 parts of mineral oil is heated at 204-227 DEG C for 5 hours. The reaction mixture is cooled to 162 DEG C and 5.3 parts of a commercial ethylene polyamine mixture having the approximate overall composition corresponding to tetraethylene pentamine is added. The reaction mixture is heated at 162-163 DEG C for 1 hour, then cooled to 130 DEG C and filtered. The filtrate is an oil solution of the desired product.

(b) A mixture is formed from 275 parts of the product solution formed as in (a), 8 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE A-47

The procedures of Examples A-1 through A-8 are repeated except that in each case a chemically equivalent amount of trimethyl borate is substituted for the boric acid, and the water used with the boric acid is omitted.

#### EXAMPLE A-48

The procedures of Examples A-1 through A-5, and A-10 through A-15 are repeated except that in each case the boronating agent consists of a chemically equivalent amount of trimethyl borate in lieu of boric acid, the water used with the boric acid is omitted, and the phosphorylating agent consists of a chemically equivalent amount of a mixture consisting of an equimolar mixture of phosphorous acid and dibutyl hydrogen phosphite.

#### EXAMPLE A-49

(a) To 120 parts of chlorinated polyisobutylene having a number average molecular weight of about 1,300 and containing about 2.8 weight percent chlorine are added 21.7 parts of pentaethylene hexamine and 5.6 parts of sodium carbonate. The reaction mixture is heated to about 205 DEG C and maintained at this temperature for about 5 hours. A stream of nitrogen is passed through the reaction mixture to remove the water of reaction. The reaction mixture is diluted with 60 parts of light mineral oil and hexane, filtered and extracted with methanol to remove excess pentaethylene hexamine. The hexane is stripped from the product by heating the mixture to 120 DEG C under a suitable vacuum. The product should have a nitrogen content of approximately 1.0 to 1.5 weight percent.

(b) A mixture is formed from 80 parts of a diluted reaction product formed as in (a), 20 parts of a 100 Solvent Neutral refined mineral oil diluent, 2.1 parts of phosphorous acid, 4.6 parts of boric acid, and 1.5 parts of water. The resultant mixture is heated at 100-105 DEG C for 2 hours and then the temperature is

gradually raised to 115 DEG C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120 DEG C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

(c) 2 Parts of powdered anhydrous boric acid is added with stirring to 80 parts of a 50 weight percent mineral oil solution of a reaction product formed as in (a) heated to 90 DEG C. The temperature of the mixture is then increased to 150 DEG C and maintained at this temperature for 4 hours while collecting the water of reaction overhead. The mixture is then filtered and mixed with 10 parts of a 100 Solvent Neutral refined mineral oil diluent, and 1.5 parts of phosphorous acid. The resultant mixture is heated at 100-105 DEG C for 2 hours and then the temperature is gradually raised to 115 DEG C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120 DEG C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

#### EXAMPLE A-50

(a) Into a reactor are placed 220 parts of p-nonylphenol and 465 parts of diethylenetriamine. The mixture is heated to 80 DEG C and 152 parts of 37% formalin is added dropwise over a period of about 30 minutes. The mixture is then heated to 125 DEG C for several hours until the evolution of water has ceased. The resultant product should contain approximately 16-20% nitrogen.

(b) Into a reactor are placed 202 parts of styrene-maleic anhydride resin (having a number average molecular weight in the range of 600-700 and a mole ratio of styrene to maleic anhydride of 1:1), 202.5 parts of octadecyl amine and 472 parts of a 95 VI lubricating oil having a viscosity at 100 DEG F of 150 SUS. The mixture is heated to 225 DEG C for several hours. To this mixture is added dropwise over a period of about 30 minutes, 85 parts of the product formed as in (a). The resulting mixture is heated for 6 hours at 210-230 DEG C while collecting the water formed during reaction. The polymeric product so formed should have a nitrogen content of about 2.1 weight percent.

(c) To a reactor are charged 200 parts of the basic nitrogen polymer produced as in (b) and 50 parts of a 100 Solvent Neutral refined mineral oil. After raising the temperature of the resulting mixture to 100-105 DEG C, 5.7 parts of boric acid, 4.0 parts of phosphorous acid, and 2.0 parts of water are added. The resultant mixture is heated at 100-105 DEG C for two hours and then the temperature is gradually raised to 115 DEG C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120 DEG C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

#### Producing Phosphorylated and Boronated Ashless Dispersants from Water and at least one Water-Hydrolyzable Organic Phosphorus Compound and at least one Boron Compound

Typical procedures for producing the phosphorylated and boronated ashless dispersants from (ii) and (iii) above involve concurrently or sequentially heating one or more ashless dispersants of the types described above with (ii) water and at least one water-hydrolyzable organic phosphorus compound and (iii) at least one boron compound under conditions yielding a liquid phosphorus- and boron-containing composition. Examples of organic phosphorus compounds which are useful in forming such products include mono-, di-, and triesters of phosphoric acid (e.g., trihydrocarbyl phosphates, dihydrocarbyl monoacid phosphates, monohydrocarbyl diacid phosphates, and mixtures thereof), mono-, di-, and triesters of phosphorous acid (e.g., trihydrocarbyl phosphites, dihydrocarbyl hydrogen phosphites, hydrocarbyl diacid phosphites, and mixtures thereof), esters of phosphonic acids (both "primary", RP(O)(OR)<sub>2</sub>, and "secondary", R<sub>2</sub>P(O)(OR)), esters of phosphinic acids, phosphonyl halides (e.g., RP(O)Cl<sub>2</sub> and R<sub>2</sub>P(O)Cl), halophosphites (e.g., (RO)PCl<sub>2</sub> and (RO)<sub>2</sub>PCl), halophosphates (e.g., ROP(O)Cl<sub>2</sub> and (RO)<sub>2</sub>P(O)Cl), tertiary pyrophosphate esters (e.g., (RO)<sub>2</sub>P(O)-O-P(O)(OR)<sub>2</sub>), and the total or partial sulfur analogs of any of the foregoing organic phosphorus compounds, and the like. Also usable, although less preferred, are the halophosphine halides (e.g., hydrocarbyl phosphorus tetrahalides, dihydrocarbyl phosphorus trihalides, and trihydrocarbyl phosphorus dihalides), and the halophosphines (monohalophosphines and dihalophosphines). By "water-hydrolyzable" is meant that the organic phosphorus compound when boiled at atmospheric pressure for a period of 5 hours with either (a) distilled water, or (b) water adjusted to at least one pH between 1 and 7 by use of H<sub>2</sub>SO<sub>4</sub>, or (c) water adjusted to at least one pH between 7 and 13 with KOH, is hydrolyzed to the extent of at least 50 mole %. In some cases, hydrolysis of certain types of organophosphorus compounds results in concomitant oxidation, and compounds which undergo both hydrolysis and oxidation under the foregoing conditions are usable in forming the phosphorylated dispersants for use in this invention. Likewise, certain sulfur-containing organophosphorus compounds undergo loss of sulfur under hydrolysis conditions. Here again, compounds of this type are suitable for use in forming the phosphorylated dispersants used in the practice of this invention. Considerable information exists in the literature concerning hydrolysis of

organophosphorus compounds – see for example Kosolapoff, Organophosphorus Compounds, John Wiley & Sons, Inc., 1950 (and pertinent references cited therein), Van Wazer, Phosphorus and its Compounds, Interscience Publishers, Inc., Vol. I: Chemistry, 1958 (and pertinent references cited therein), and Vojvodic, et al, Arch. Belg. Med. Soc., Hyg., Med. Trav. Med. Leg., Suppl. (Proc.-World Congr. "New Compd. Biol. Chem. Warf.: Tox Eval.", 1st, 1984), pp. 49-52. The preferred water-hydrolyzable organic phosphorus compounds are the water-hydrolyzable phosphate esters, and the water-hydrolyzable phosphite esters, especially the dihydrocarbyl hydrogen phosphites.

Optionally, additional sources of basic nitrogen can be included in the organic phosphorus compound-ashless dispersant-boron compound-water mixture so as to provide a molar amount (atomic proportion) of basic nitrogen up to that equal to the molar amount of basic nitrogen contributed by the ashless dispersant. Preferred auxiliary nitrogen compounds are long chain primary, secondary and tertiary alkyl amines containing from about 12 to 24 carbon atoms, including their hydroxyalkyl and aminoalkyl derivatives. The long chain alkyl group may optionally contain one or more ether groups. Examples of suitable compounds are oleyl amine, N-oleyltrimethylene diamine, N-tallow diethanolamine, N,N-dimethyl oleylamine, and myristyloxapropyl amine.

Other materials normally used in lubricant additives which do not interfere with the process may also be added, for example, a benzotriazole, including lower (C1-C4) alkyl-substituted benzotriazoles, which function to protect copper surfaces.

The concurrent heating step or the combination of sequential heating steps is conducted at temperatures sufficient to produce a final liquid composition which contains both phosphorus and boron. The heating can be carried out in the absence of a solvent by heating a mixture of the ashless dispersant, water and one or more suitable organic phosphorus compounds, or one or more suitable boron compounds, or, preferably, a combination of water, one or more suitable organic phosphorus compounds and one or more suitable boron compounds. The temperatures used will vary somewhat depending upon the nature of the ashless dispersant and the organic phosphorus and/or boron reagent being utilized. Generally speaking however, the temperature will usually fall within the range of about 40 to about 200 DEG C. The duration of the heating is likewise susceptible to variation, but ordinarily will fall in the range of about 1 to about 3 hours. When conducting the heating in bulk, it is important to thoroughly agitate the components to insure intimate contact therebetween. When utilizing the preferred boron reagent (boric acid) in a boronation conducted separately from the phosphorylation, it is preferable to add water with the boric acid to facilitate initial dissolution of the boric acid.

Various methods can be used for removing water from component b) during or after its formation. The preferred method involves applying a suitable vacuum to the reaction system while heating the water-containing mixture to a suitably elevated temperature. In this way the water is readily stripped off. When conducting the phosphorylation (separately or concurrently with boronation) using a phosphorus ester made from a lower alcohol such as methanol, ethanol, propanol, 2-propanol, butanol, isobutyl alcohol, etc., both lower alcohol liberated in the process and water can be stripped off from the product mixture during or on completion of the heating operation. For example, water and relatively volatile alcohols formed in the hydrolysis process and the added water are preferably removed from the heated mixture by vacuum distillation at temperatures of from about 100 to about 140 DEG C. Preferably the heating step or steps will be conducted in a diluent oil or other inert liquid medium such as light mineral oils, and the like.

The amount of phosphorus compound employed in the heating process ranges from about 0.001 mole to 0.999 mole per mole of basic nitrogen and free hydroxyl in the mixture being heated, up to one half of which may be contributed by an auxiliary nitrogen compound. The amount of boron compound employed ranges from about 0.001 mole to about 1 mole per mole of basic nitrogen and/or hydroxyl in the mixture which is in excess of the molar amount of inorganic phosphorus compound. When conducting the phosphorylation and boronation on a sequential basis (or when conducting one of these operations on a dispersant which has previously been subjected to the other such operation), the last-to-be-used reagent(s) — water and organic phosphorus compound(s) or boron compound(s), as the case may be — can be used in an amount equivalent to (or even in excess of) the amount of basic nitrogen and/or hydroxyl groups in the dispersant being heated with such last-to-be-used reagent(s).

As noted above, insofar as the phosphorylation is concerned, it is preferable to heat the ashless dispersant with one or more water-hydrolyzable organic phosphorus compounds in the presence of water. In this case the water can be added before and/or during the heating step, and before, after, or at the same time one or more phosphorus compounds are introduced into the vessel in which the heating is taking place or is to take place. It is also possible to heat the ashless dispersant with the organic phosphorus compound and then subsequently heat the resultant composition with water, although this procedure is less preferred.

The amount of added water is not particularly critical as long as a sufficient amount is present to effect hydrolysis of the water-hydrolyzable organic phosphorus compound. Water present in the system can be

removed by distillation (preferably at reduced pressure) during the course of, and preferably is removed at the end of, the heating step. Amounts of water up to 15% by weight of the mixture being heated are preferred, and amounts of water of up to 5% by weight are particularly preferred. When used, the amount of diluent usually ranges from about 10 to about 50% by weight of the mixture being subjected to heating.

The hydrolysis of the water-hydrolyzable organic phosphorus compound(s) employed in the phosphorylation operation can be effected in any of a variety of ways. For example, the dispersant to be phosphorylated, one or more water-hydrolyzable organic phosphorus compounds, and water may be mixed together and heated either in an open system at atmospheric pressure or in a closed system at superatmospheric pressure. If conducted with an open system, the temperature may be kept below the boiling point of water and the mixture subjected to stirring of sufficient intensity to cause and maintain intimate contact among the components within the hydrolysis reaction mixture. It is also feasible to raise the temperature of the mixture in an open system to the boiling point of water and allow the water vapor either to escape from the system or to be condensed in a suitable condensing system and returned to the refluxing hydrolysis reaction mixture. If the water is allowed to escape, sufficiently large amounts of water should be used to insure that a substantial amount of hydrolysis occurs before the supply of water in the hydrolysis mixture has been depleted. In all such cases, water can be fed to the system as an initial complete charge or it can be fed intermittently or continuously into the hydrolysis mixture.

When conducting the hydrolysis in a closed system, the system may be kept at one or more selected autogenous pressures by suitable adjustment and regulation of the temperature. And, still higher pressures may be imposed upon the system, as for example by injecting high pressure steam into a sealed autoclave containing the hydrolysis reaction mixture.  
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The water itself may be charged to the system in any suitable form, such as in the form of liquid water, steam, or even ice. Similarly, the water may be introduced in the form of hydrated solids so that the water is released by the application of heat during the course of the hydrolysis operation. Injection of wet steam into a well-agitated hydrolysis system is one preferred way of conducting the operation.

The hydrolysis operation should be conducted under any given set or sequence of hydrolysis conditions for a period of time long enough that at least 10%, preferably at least 50%, and most preferably at least 75%, of the organic phosphorus compound(s) present in the hydrolysis mixture have been hydrolyzed. The nature of the hydrolysis products can be expected to vary in relation to the type of phosphorus compound(s) used and the severity of the hydrolysis conditions imposed upon the hydrolysis system. Thus inorganic and organic hydrolysis products can be formed in the system, and these in turn can be expected to be taken up by the ashless dispersant(s) present in the system substantially as they are formed. Accordingly, although the chemical structure(s) of the phosphorylated dispersant(s) are not known with absolute certainty, it is reasonable to conclude that at least some interaction occurs between the dispersant(s) and organic and/or inorganic phosphorus-containing species formed in the hydrolysis reactions taking place in the system. It is also conceivable that such interacted components may undergo displacements and/or other forms of interactions with components present in the hydrolysis system as the hydrolysis operation proceeds.

As pointed out above, the phosphorylation may be conducted apart from the boronation, or it may be conducted concurrently with the boronation. When performing the phosphorylation and boronation operations concurrently, any of the foregoing hydrolysis procedures can be utilized, the principal difference being that one or more boron compounds are used in combination with one or more water-hydrolyzable organic phosphorus compounds.

If desired, small amounts of one or more acids (e.g., sulfuric acid, phosphoric acid, phosphorous acid, etc.) or bases (e.g., NaOH, KOH, ammonium hydroxide, etc.) may be added to the hydrolysis mixture to facilitate hydrolysis of the organic phosphorus compound(s) being used.

When forming component b) in part by use of one or more inorganic phosphorus compounds such as phosphorous acid ( $H_3PO_3$ , sometimes depicted as  $H_2(HPO_3)$ , and sometimes called orthophosphorous acid or phosphonic acid), phosphoric acid ( $H_3PO_4$ , sometimes called orthophosphoric acid), hypophosphorous acid ( $H_3PO_2$ , sometimes called phosphinic acid), hypophosphoric acid ( $H_4P_2O_6$ ), metaphosphoric acid ( $HPO_3$ ), pyrophosphoric acid ( $H_4P_2O_7$ ), pyrophosphorous acid ( $H_4P_2O_5$ , sometimes called pyrophosphonic acid), phosphinous acid ( $H_3PO$ ), tripolyphosphoric acid ( $H_5P_3O_10$ ), tetrapolyphosphoric acid ( $H_6P_4O_{13}$ ), trimetaphosphoric acid ( $H_3P_3O_9$ ), phosphorus trioxide, phosphorus tetraoxide, phosphorus pentoxide, and/or partial or total sulfur analogs of the foregoing such as phosphorotetrathioic acid ( $H_3PS_4$ ), phosphoromonothioic acid ( $H_3PO_3S$ ), phosphorodithioic acid ( $H_3PO_2S_2$ ), phosphorotrithioic acid ( $H_3POS_3$ ), phosphorus sesquisulfide, phosphorus heptasulfide, and phosphorus pentasulfide ( $P_2S_5$ , sometimes referred to as  $P_4S_{10}$ ), or the like, and in part by use of one or more water-hydrolyzable organic phosphorus compounds, the latter should be used in an amount sufficient to provide at least 10% (preferably at least 50% and more preferably at least 75%) of the total phosphorus content of the phosphorylated and boronated dispersant. For crankcase lubricant usage,

component b) when in the undiluted state preferably contains at least 3000 ppm (more preferably at least 5000 ppm and most preferably at least 7000 ppm) of phosphorus and at least 1500 ppm (more preferably at least 2500 ppm and most preferably at least 3500 ppm) of boron.

The preparation of phosphorylated and boronated ashless dispersants suitable for use as component b) in the compositions of this invention from (ii) and (iii) above is illustrated by the following examples in which all parts and percentages are by weight unless otherwise clearly specified.

#### EXAMPLE B-1

A mixture is formed from 260 parts of a commercial succinimide ashless dispersant (HiTEC TM 644 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.), 100 parts of a 100 Solvent Neutral refined mineral oil diluent, 26 parts of dibutyl hydrogen phosphite, 3.5 parts of tolutriazole, 10 parts of boric acid, and 8 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water and butanol while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE B-2

The procedure of Example B-1 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 1,100. The average number of succinic groups per alkenyl group in the succinimide is approximately 1.2.

#### EXAMPLE B-3

The procedure of Example B-1 is repeated except that the succinimide ashless dispersant used is derived from polybutene having a number average molecular weight of 2,100.

#### EXAMPLE B-4

The procedure of Example B-1 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a Mannich polyamine dispersant (AMOCO TM 9250 dispersant; Amoco Corporation). The Amoco 9250 dispersant as supplied by the manufacturer is believed to be a boronated dispersant and in such case, another material suitable for use as component b) can be formed by eliminating the boric acid from the procedure used in this example and thereby conducting phosphorylation on an already boronated dispersant.

#### EXAMPLE B-5

The procedure of Example B-1 is repeated except that the succinimide ashless dispersant is replaced by an equal amount of a commercial ashless dispersant of the pentaerythritol succinester type (Lubrizol TM 936 dispersant; The Lubrizol Corporation). As in the case of Example B-4, the initial dispersant as supplied by the manufacturer is believed to be a boronated dispersant. In such cases, the dispersant can, if desired, be subjected just to phosphorylation to thereby form still another product suitable for use as component b).

#### EXAMPLE B-6

The procedure of Example B-1 is repeated except that 16 parts of trimethyl phosphite is used in place of the dibutyl hydrogen phosphite, to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE B-7

The procedure of Example B-1 is repeated except that the dibutyl hydrogen phosphite is replaced by 16.3 parts of O-ethyl-O,O-1,2-ethanediyl phosphite.

#### EXAMPLE B-8

The procedures of Examples B-1 through B-7 are repeated except that the tolutriazole is omitted from the initial mixtures subjected to the thermal processes.

#### EXAMPLE B-9

A mixture of 12,000 parts of a commercial boronated succinimide (HiTEC TM 648 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.), 90 parts of water, and 584 parts of triphenylmethane phosphonyl dichloride is heated to 100-110 DEG C for 6 hours while sweeping the reaction mixture with nitrogen. A vacuum of 40 mm Hg is then gradually applied to remove water and thereby form a homogeneous liquid composition suitable for use as component b) in the practice of this invention. For convenience in handling, 100 Solvent Neutral mineral oil can be added to form an 80% solution of the additive in the oil.  
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#### EXAMPLE B-10

A mixture of 260 parts of a commercial succinimide (HiTEC TM 644 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.), 3 parts of water, 13 parts of tributyl phosphate, and 4 parts of phosphorous acid is heated to 100 DEG C for 2 hours. To this product is added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100 DEG C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 110 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE B-11

A mixture of 260 parts of a commercial succinimide (HiTEC TM 644 dispersant; Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.), 8 parts of orthoboric acid and 4 parts of water is heated to 100 DEG C for 2 hours. Then 16 parts of diethyl hydrogen phosphite and 6 parts of aqueous ammonium hydroxide (3N) are added to the reaction mixture and the temperature of the mixture is held at 100 DEG C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 110 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE B-12

A mixture of 260 parts of a commercial succinic pentaerythritol ester ashless dispersant (Lubrizol TM 936 dispersant; The Lubrizol Corporation), 6 parts of water, and 16 parts of methyl dichlorophosphate is heated to 100 DEG C for 2 hours. To this product are added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100 DEG C for another 2 hours. The mixture is then swept with nitrogen for one hour at 100 DEG C. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 110 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE B-13

A mixture of 260 parts of a commercial succinic pentaerythritol ester ashless dispersant (Lubrizol TM 936 dispersant; The Lubrizol Corporation), 8 parts of orthoboric acid and 6 parts of water is heated to 100 DEG C for 2 hours. Then 19 parts of methyl bis(phenyl) phosphate, 5 parts of phosphoric acid, and 0.4 part of additional water are added to the reaction mixture and the temperature of the mixture is held at 100 DEG

C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 130 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE B-14

A mixture of 260 parts of a commercial Mannich polyamine dispersant (AMOCO TM 9250 dispersant; Amoco Corporation), 8 parts of water, and 35 parts of dibenzyl methyl phosphate is heated to 100 DEG C for 2 hours. To this product is added 8 parts of orthoboric acid and 4 parts of water, and the resultant mixture is heated at 100 DEG C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 130 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE B-15

A mixture of 260 parts of a commercial Mannich polyamine dispersant (AMOCO TM 9250 dispersant; Amoco Corporation), parts of orthoboric acid and 4 parts of water is heated to 100 DEG C for 2 hours. Then 9 parts of monophenyl phosphate, 4 parts of phosphorous acid, and an additional 3 parts of water are added to the reaction mixture and the temperature of the mixture is held at 100 DEG C for another 2 hours. A vacuum of 40 mm of Hg is applied to the system and the temperature is gradually raised to 130 DEG C. The resultant homogeneous liquid composition is suitable for use as component b) in the practice of this invention.

#### EXAMPLE B-16

- (a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutylene succinic anhydride acylating agent.  
(b) A mixture is prepared by the addition of 57 parts (1.38 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 1,067 parts of mineral oil and 893 parts (1.38 equivalents) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140-145 DEG C. The reaction mixture is then heated to 155 DEG C over a three hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominantly of polyisobutylene succinimides.  
(c) A mixture is formed from 250 parts of the polyisobutylene succinimide product solution formed as in (b), 11 parts of dibutyl chlorophosphate, 5 parts of phosphoric acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100 DEG C for four hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE B-17

The procedure of Example B-16 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE B-18

The procedure of Example B-16 is repeated except that 9 parts of an equimolar mixture of dibutyl hydrogen phosphite and monobutyl dihydrogen phosphite is used in place of the dibutyl chlorophosphate to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE B-19

The procedure of Example B-16 is repeated except that the dibutyl chlorophosphate is replaced by 11 parts of mono-2-naphthyl orthophosphate.

#### EXAMPLE B-20

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutetyl succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 18.2 parts (0.433 equivalents) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 392 parts of mineral oil and 348 parts (0.52 equivalent) of substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 140 DEG C. The reaction mixture is then heated to 150 DEG C in 1.8 hours and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired product composed predominantly of polyisobutetyl succinimides.

(c) A mixture is formed from 250 parts of the polyisobutetyl succinimide product solution formed as in (b), 18 parts of phenyl dimethyl phosphate, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100 DEG C for three hours. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 130 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE B-21

The procedure of Example B-20 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE B-22

The procedure of Example B-20 is repeated except that 15 parts of trimethyl phosphite is used in place of the phenyl dimethyl phosphate to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE B-23

The procedure of Example B-20 is repeated except that the phenyl dimethyl phosphate is replaced by 36 parts of 4-dimethyl-aminophenyl phosphorus tetrachloride and the heated mixture in (c) is swept with nitrogen during the three-hour period.

#### EXAMPLE B-24

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutetyl succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier (Dow Chemical Company) is heated at 150 DEG C for 2.5 hours. The reaction mixture is then heated to 210 DEG C over a period of 5 hours and then held at 210 DEG C for an additional 3.2 hours. The reaction mixture is cooled to 190 DEG C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205 DEG C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 37 parts

of bis-(2-ethylhexyl) hydrogen phosphite, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 130 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE B-25

The procedure of Example B-24 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE B-26

The procedure of Example B-24 is repeated except that 26 parts of dibutyl hydrogen phosphite is used in place of the bis(2-ethylhexyl) hydrogen phosphite to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE B-27

The procedure of Example B-24 is repeated except that the bis(2-ethylhexyl) hydrogen phosphite is replaced by 15 parts of trimethyl phosphite.

#### EXAMPLE B-28

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutylene succinic anhydride acylating agent.

(b) A mixture of 3225 parts (5.0 equivalents) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 289 parts (8.5 equivalents) of pentaerythritol and 5204 parts of mineral oil is heated at 225-235 DEG C for 5.5 hours. The reaction mixture is filtered at 130 DEG C to yield an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 300 parts of the ashless dispersant product solution formed as in (b), 27 parts of dibutyl chlorophosphate, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE B-29

The procedure of Example B-28 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE B-30

The procedure of Example B-28 is repeated except that 8 parts of ethyl dichlorophosphate and 4 parts of phosphorous acid are used in place of the dibutyl chlorophosphate to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE B-31

The procedure of Example B-28 is repeated except that the dibutyl chlorophosphate is replaced by 10

parts of dibutyl hydrogen phosphite and 5 parts of phosphoric acid.

#### EXAMPLE B-32

(a) A mixture of 1,000 parts (0.495 mole) of polyisobutene ( $M_n = 2020$ ;  $M_w = 6049$ , both as per U.S. Pat. No. 4,234,435) and 115 parts (1.17 moles) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 184 DEG C in 6 hours during which 85 parts (1.2 moles) of gaseous chlorine is added beneath the surface. At 184-189 DEG C, an additional 59 parts (0.83 mole) of chlorine is added over 4 hours. The reaction mixture is stripped by heating at 186-190 DEG C with nitrogen purged for 26 hours. The residue is predominantly polyisobutylene succinic anhydride acylating agent.

(b) A mixture of 322 parts (0.5 equivalent) of the polyisobutene-substituted succinic acylating agent prepared as in (a), 68 parts (2.0 equivalents) of pentaerythritol and 508 parts of mineral oil is heated at 204-227 DEG C for 5 hours. The reaction mixture is cooled to 162 DEG C and 5.3 parts (0.13 equivalent) of a commercial ethylene polyamine mixture having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is heated at 162-163 DEG C for 1 hour, then cooled to 130 DEG C and filtered. The filtrate is an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 350 parts of the ashless dispersant product solution formed as in (b), 16 parts of diethyl hydrogen phosphite, 3.5 parts of tolutriazole, 8 parts of boric acid, and 6 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE B-33

The procedure of Example B-32 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE B-34

The procedure of Example B-32 is repeated except that 20 parts of diethyl chlorophosphate is used in place of the diethyl hydrogen phosphite to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE B-35

The procedure of Example B-32 is repeated except that the diethyl hydrogen phosphite is replaced by 12 parts of ethyl dibutyl phosphate and 4 parts of phosphorous acid.

#### EXAMPLE B-36

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ( $M_n = 1845$ ;  $M_w = 5325$ , both as per U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 190 DEG C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192 DEG C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193 DEG C with nitrogen blowing for 10 hours. The residue is predominantly polyisobutylene succinic anhydride acylating agent.

(b) A mixture of 334 parts (0.52 equivalents) of the polyisobutene substituted succinic acylating agent prepared as in (a), 548 parts of mineral oil, 30 parts (0.88 equivalent) of pentaerythritol and 8.6 parts (0.0057 equivalent) of Polyglycol 112-2 demulsifier (Dow Chemical Company) is heated at 150 DEG C for 2.5 hours. The reaction mixture is then heated to 210 DEG C over a period of 5 hours and then held at 210 DEG C for an additional 3.2 hours. The reaction mixture is cooled to 190 DEG C and 8.5 parts (0.2 equivalent) of a commercial mixture of ethylene polyamines having an overall composition approximating that of tetraethylene pentamine is added. The reaction mixture is stripped by heating at 205 DEG C with nitrogen blowing for 3 hours, and then filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 260 parts of the ashless dispersant product solution formed as in (b), 20 parts of ethyl dichloro phosphate, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40

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mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE B-37

The procedure of Example B-36 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE B-38

The procedure of Example B-36 is repeated except that 23 parts of butyl dichloro phosphate is used in place of the ethyl dichloro phosphate to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE B-39

The procedure of Example B-36 is repeated except that the ethyl dichloro phosphate is replaced by 30 parts of mono-butyl-mono-2-ethylhexyl hydrogen phosphite.

#### EXAMPLE B-40

(a) A mixture of 510 parts (0.28 mole) of polyisobutene ( $M_n = 1845$ ;  $M_w = 5325$ , both as per U.S. Pat. No. 4,234,435) and 59 parts (0.59 mole) of maleic anhydride is heated to 110 DEG C. This mixture is heated to 190 DEG C in 7 hours during which 43 parts (0.6 mole) of gaseous chlorine is added beneath the surface. At 190-192 DEG C, an additional 11 parts (0.16 mole) of chlorine is added over 3.5 hours. The reaction mixture is stripped by heating at 190-193 DEG C with nitrogen blowing for 10 hours. The residue is predominantly polyisobutylene succinic anhydride acylating agent.

(b) A mixture is prepared by the addition of 10.2 parts (0.25 equivalent) of a commercial mixture of ethylene polyamines having the approximate overall composition of tetraethylene pentamine to 113 parts of mineral oil and 161 parts (0.25 equivalent) of the substituted succinic acylating agent prepared as in (a) while maintaining the temperature at 138 DEG C. The reaction mixture is heated to 150 DEG C over a 2 hour period and stripped by blowing with nitrogen. The reaction mixture is filtered to yield the filtrate as an oil solution of the desired ashless dispersant product.

(c) A mixture is formed from 125 parts of the polyisobutylene succinimide product solution formed as in (b), 9 parts of monobenzyl phosphate and 4 parts of phosphorous acid, 3.5 parts of tolutriazole, 8 parts of boric acid, and 6 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE B-41

The procedure of Example B-40 is repeated except that the tolutriazole is eliminated from the reaction mixture of (c).

#### EXAMPLE B-42

The procedure of Example B-40 is repeated except that 14 parts of dibenzyl phosphate is used in place of the monobenzyl phosphate to provide a clear, oil-soluble composition suitable for use as component b).

#### EXAMPLE B-43

The procedure of Example B-40 is repeated except that the monobenzyl phosphate is replaced by 17

parts of monophenyl dibenzyl phosphate.

#### EXAMPLE B-44

To a reactor are charged under a nitrogen atmosphere 67.98 parts of a commercially-available polyisobutylene succinimide of a mixture of polyethylene polyamines having the approximate overall composition of tetraethylene pentamine (the polyisobutylene group derived from polyisobutene having a number average molecular weight of about 900; the succinimide product having a ratio of about 1.15 succinic groups per alkenyl group) and 26.14 parts of a 100 Solvent neutral refined mineral oil. After raising the temperature of the resulting solution to 100-105 DEG C, 2.09 parts of boric acid and 4.6 parts of dibutyl hydrogen phosphite are introduced into the reactor, followed by 0.92 part of tolutriazole (Cobratec TT-100; PMC Specialties Group, Cincinnati, Ohio) and then 3 parts of water. The resultant mixture is heated at 100-105 DEG C for two hours and then the temperature is gradually raised to 115 DEG C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120 DEG C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

#### EXAMPLE B-45

) The procedure of Example B-44 is repeated except that the tolutriazole is omitted from the reaction mixture.

#### EXAMPLE B-46

(a) A mixture of 322 parts of the polyisobutene-substituted succinic acylating agent made as in Example B-40(a), 68 parts of pentaerythritol and 508 parts of mineral oil is heated at 204-227 DEG C for 5 hours. The reaction mixture is cooled to 162 DEG C and 5.3 parts of a commercial ethylene polyamine mixture having the approximate overall composition corresponding to tetraethylene pentamine is added. The reaction mixture is heated at 162-163 DEG C for 1 hour, then cooled to 130 DEG C and filtered. The filtrate is an oil solution of the desired product.

(b) A mixture is formed from 275 parts of the product solution formed as in (a), 20 parts of diisopropyl hydrogen phosphite, 3.5 parts of tolutriazole, 8 parts of boric acid, and 8 parts of water. The mixture is heated at 100 DEG C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to remove the water while the temperature is slowly raised to 100 DEG C. A clear solution or composition is obtained which is soluble in oil and suitable for use as component b).

#### EXAMPLE B-47

The procedures of Examples B-1 through B-8 are repeated except that in each case a chemically equivalent amount of trimethyl borate is substituted for the boric acid.

#### EXAMPLE B-48

The procedures of Examples B-1 through B-5, and B-10 through B-15 are repeated except that in each case the boronating agent consists of a chemically equivalent amount of trimethyl borate in lieu of boric acid, and the phosphorylating agent consists of a chemically equivalent amount of a mixture consisting of an equimolar mixture of phosphorous acid and dibutyl hydrogen phosphite.

#### EXAMPLE B-49

(a) To 120 parts of chlorinated polyisobutylene having a number average molecular weight of about 1,300 and containing about 2.8 weight percent chlorine are added 21.7 parts of pentaethylene hexamine and 5.6 parts of sodium carbonate. The reaction mixture is heated to about 205 DEG C and maintained at this temperature for about 5 hours. A stream of nitrogen is passed through the reaction mixture to remove the water of reaction. The reaction mixture is diluted with 60 parts of light mineral oil and hexane, filtered and extracted with methanol to remove excess pentaethylene hexamine. The hexane is stripped from the

product by heating the mixture to 120 DEG C under a suitable vacuum. The product should have a nitrogen content of approximately 1.0 to 1.5 weight percent.

(b) A mixture is formed from 80 parts of a diluted reaction product formed as in (a), 20 parts of a 100 Solvent Neutral refined mineral oil diluent, 5.0 parts of dibutyl hydrogen phosphite, 4.6 parts of boric acid, and 3.0 parts of water. The resultant mixture is heated at 100-105 DEG C for 2 hours and then the temperature is gradually raised to 115 DEG C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120 DEG C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

(c) 2 Parts of powdered anhydrous boric acid is added with stirring to 80 parts of a 50 weight percent mineral oil solution of a reaction product formed as in (a) heated to 90 DEG C. The temperature of the mixture is then increased to 150 DEG C and maintained at this temperature for 4 hours while collecting the water of reaction overhead. The mixture is then filtered and mixed with 10 parts of a 100 Solvent Neutral refined mineral oil diluent, 3.6 parts of dibutyl hydrogen phosphite and 3.0 parts of water. The resultant mixture is heated at 100-105 DEG C for 2 hours and then the temperature is gradually raised to 115 DEG C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120 DEG C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

**EXAMPLE B-50**

(a) Into a reactor are placed 220 parts of p-nonyl-phenol and 465 parts of diethylenetriamine. The mixture is heated to 80 DEG C and 152 parts of 37% formalin is added dropwise over a period of about 30 minutes. The mixture is then heated to 125 DEG C for several hours until the evolution of water has ceased. The resultant product should contain approximately 16-20% nitrogen.

(b) Into a reactor are placed 202 parts of styrenemaleic anhydride resin (having a number average molecular weight in the range of 600-700 and a mole ratio of styrene to maleic anhydride of 1:1), 202.5 parts of octadecyl amine and 472 parts of a 95 VI lubricating oil having a viscosity at 100 DEG F of 150 SUS. The mixture is heated to 225 DEG C for several hours. To this mixture is added dropwise over a period of about 30 minutes, 85 parts of the product formed as in (a). The resulting mixture is heated for 6 hours at 210-230 DEG C while collecting the water formed during reaction. The polymeric product so formed should have a nitrogen content of about 2.1 weight percent.

formed should have a nitrogen content of about 2.1 weight percent.

(c) To a reactor are charged 250 parts of the basic nitrogen polymer produced as in (b) and 50 parts of a 100 Solvent Neutral refined mineral oil. After raising the temperature of the resulting mixture to 100-105 DEG C, 5.7 parts of boric acid, 35 parts of dibutyl hydrogen phosphite, and 8 parts of water are added. The resultant mixture is heated at 100-105 DEG C for two hours and then the temperature is gradually raised to 115 DEG C with the application of a vacuum to 40 mm Hg. Stripping is continued for 90 minutes and until 120 DEG C/40 mm Hg has been reached. A flow of dry nitrogen is then applied to the system and the product mixture is allowed to cool. The product mixture is suitable for use as component b) in the compositions of this invention.

**EXAMPLE B-51**

The procedure of Example B-32 is repeated except that the dibutyl hydrogen phosphite is replaced by 10 parts of dimethyl hydrogen phosphite.

**EXAMPLE B-52**

The procedure of Example B-32 is repeated except that the diethyl hydrogen phosphite is replaced by 5 parts of dimethyl hydrogen phosphite and 4 parts of phosphorous acid.

A particularly preferred embodiment of this invention involves using as component b) a phosphorylated and boronated alkenyl succinimide of a polyethylene polyamine or mixture of polyethylene polyamines, wherein the succinimide is formed from (i) an alkenyl succinic acylating agent having a succination ratio (i.e., the ratio of the average number of chemically bound succinic groups per alkenyl group in the molecular structure of the succinic acylating agent) in the range of 1 to about 1.3, the alkenyl group being derived from a polyolefin (most preferably a polyisobutene) having a number average molecular weight in the range of about 600 to about 1,300 (more preferably in the range of 700 to 1,250 and most preferably in the range of 800 to 1,200).

Unless otherwise expressly indicated, the following procedures are used to determine the succinyl ratio

of the alkenyl succinic acylating agents utilized in forming such particularly preferred phosphorylated and boronated ashless dispersants:

A. The number average molecular weight ( $M_n$ ) of the polyalkene from which the substituent is derived is determined by use of either of two methods, namely, vapor pressure osmometry (VPO) or gel permeation chromatography (GPC). The VPO determination should be conducted in accordance with ASTM D2503-82 using high purity toluene as the measuring solvent.

Alternatively, a GPC procedure can be employed. As is well known, the GPC technique involves separating molecules according to their size in solution. For this purpose liquid chromatographic columns are packed with a styrene-divinyl benzene copolymer of controlled particle and pore sizes. When the polyalkene molecules from which the substituent is derived are transported through the GPC columns by a solvent (tetrahydrofuran), the polyalkene molecules small enough to penetrate into the pores of the column packing are retarded in their progress through the columns. On the other hand, the polyalkene molecules which are larger either penetrate the pores only slightly or are totally excluded from the pores. As a consequence, these larger polyalkene molecules are retarded in their progress through the columns to a lesser extent. Thus a velocity separation occurs according to the size of the respective polyalkene molecules. In order to define the relationship between polyalkene molecular weight and elution time, the GPC system to be used is calibrated using known molecular weight polyalkene standards and an internal standard method. Details concerning such GPC procedures and methods for column calibration are extensively reported in the literature. See for example, W. W. Yau, J. J. Kirkland, and D. D. Bly, Modern Size-Exclusion Liquid Chromatography, John Wiley & Sons, 1979, Chapter 9 (pages 285-341), and references cited therein.

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In general, the  $M_n$  determined by the VPO and GPC methods should agree within the precision of the respective methods.

B. The total weight of the substituent groups present in the substituted succinic acylating agent is determined by conventional methods for determination of the number of carbonyl functions. The preferred procedure for use involves non-aqueous titration of the substituted acylating agent with standardized sodium isopropoxide. In this procedure the titration is conducted in a 1:1 mineral spirits:1-butanol solvent system. An alternative, albeit less preferred, procedure is the ASTM D-94 procedure.

The results from procedures A and B above are used in calculating the weight of substituent groups per unit weight of total sample.

C. In determining the succination ratio of the alkenyl succinic acylating agents used in forming the particularly preferred phosphorylated and boronated ashless dispersants employed as component b) pursuant to this invention, the determination is to be based on the active portion of the sample. That is to say, alkenyl succinic acylating agents are often produced as a mixture with an inactive diluent. Thus for the purpose of succination ratio determination, such diluent should not be considered a part of the succinic acylating agent, and accordingly a separation as between the diluent and the alkenyl succinic acylating agent should be accomplished. Such separation can be effected before determination of total weight of the substituent groups present in the substituted succinic acylating agent. However, it is preferable to effect such separation after such determination using a mathematical correction of the result. The separation itself can be achieved using a silica gel column separation technique. A low molecular weight non-polar hydrocarbon solvent, such as hexane and more preferably pentane, is used as the solvent whereby the unreactive diluent is readily eluted from the column. The substituted succinic acylating agent entrained in the column can then be recovered by use of a more polar elution solvent, preferably methanol/methylene dichloride.

#### Component c)

The metal-containing detergents which preferably are employed in conjunction with components a) and b) of the compositions of this invention are exemplified by oil-soluble basic salts of alkali or alkaline earth metals with one or more of the following acidic substances (or mixtures thereof): (1) sulfonic acids, (2) carboxylic acids, (3) salicylic acids, (4) alkylphenols, (5) sulfurized alkylphenols, (6) organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage. Such organic phosphorus acids include those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium. The salts for use as component c) should be basic salts having a TBN of at least 50, preferably above 100, and most preferably above 200.

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The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature of about 50 DEG C, and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve alcohol, Carbitol alcohol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, piperidinediamine, phenothiazine, phenyl-beta-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60 DEG -200 DEG C.

Examples of suitable metal-containing detergents include, but are not limited to, the basic or overbased salts of such substances as lithium phenates, sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulfurized lithium phenates, sulfurized sodium phenates, sulfurized potassium phenates, sulfurized calcium phenates, and sulfurized magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility; lithium sulfonates, sodium sulfonates, potassium sulfonates, calcium sulfonates, and magnesium sulfonates wherein each sulfonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; lithium salicylates, sodium salicylates, potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility; the lithium, sodium, potassium, calcium and magnesium salts of hydrolysed phosphosulfurized olefins having 10 to 2000 carbon atoms or of hydrolyzed phosphosulfurized alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2000 carbon atoms; lithium, sodium, potassium, calcium and magnesium salts of aliphatic carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids; and many other similar alkali and alkaline earth metal salts of oil-soluble organic acids. Mixtures of basic or overbased salts of two or more different alkali and/or alkaline earth metals can be used. Likewise, basic or overbased salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more calcium phenates with one or more calcium sulfonates) can also be used. While rubidium, cesium and strontium salts are feasible, their expense renders them impractical for most uses. Likewise, while barium salts are effective, the status of barium as a heavy metal under a toxicological cloud renders barium salts less preferred for present-day usage.

As is well known, overbased metal detergents are generally regarded as containing overbasing quantities of inorganic bases, probably in the form of micro dispersions or colloidal suspensions. Thus the term "oil-soluble" as applied to component c) materials is intended to include metal detergents wherein inorganic bases are present that are not necessarily completely or truly oil-soluble in the strict sense of the term, inasmuch as such detergents when mixed into base oils behave in much the same way as if they were fully and totally dissolved in the oil.

Collectively, the various basic or overbased detergents referred to hereinabove, have sometimes been called, quite simply, basic alkali metal or alkaline earth metal-containing organic acid salts.

Methods for the production of oil-soluble basic and overbased alkali and alkaline earth metal-containing detergents are well known to those skilled in the art and are extensively reported in the patent literature. See for example, the disclosures of U.S. Pat. Nos. 2,451,345; 2,451,346; 2,485,861; 2,501,731; 2,501,732; 2,585,520; 2,671,758; 2,616,904; 2,616,905; 2,616,906; 2,616,911; 2,616,924; 2,616,925; 2,617,049; 2,695,910; 3,178,368; 3,367,867; 3,496,105; 3,629,109; 3,865,737; 3,907,691; 4,100,085; 4,129,589; 4,137,184; 4,148,740; 4,212,752; 4,617,135; 4,647,387; 4,880,550; GB Published Patent Application 2,082,619 A, and European Patent Application Publication Nos. 121,024 B1 and 259,974 A2.

The basic or overbased metal detergents utilized as component c) can, if desired, be oil-soluble boronated alkali or alkaline earth metal-containing detergents. Methods for preparing boronated, overbased metal detergents are described, for example, in U.S. Pat. Nos. 3,480,548; 3,679,584; 3,829,381; 3,909,691; 4,965,003; and 4,965,004.

Particularly preferred metal detergents for use as component c) are one or more calcium sulfonates, one or more magnesium sulfonates, or combinations of one or more calcium sulfonates and one or more magnesium sulfonates. Most preferred are one or more overbased calcium sulfonates, one or more overbased magnesium sulfonates, and combinations of one or more overbased calcium sulfonates and one or more overbased magnesium sulfonates.

#### Other Additive Components

The lubricant and lubricant concentrates of this invention can and preferably will contain additional components in order to partake of the properties which can be conferred to the overall composition by such additional components. The nature of such components will, to a large extent, be governed by the particular use to which the ultimate oleaginous composition (lubricant or functional fluid) is to be subjected.

#### Antioxidants.

Most oleaginous compositions will contain a conventional quantity of one or more antioxidants in order to protect the composition from premature degradation in the presence of air, especially at elevated temperatures. Typical antioxidants include hindered phenolic antioxidants, secondary aromatic amine antioxidants, sulfurized phenolic antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, and the like.

Illustrative sterically hindered phenolic antioxidants include ortho-alkylated phenolic compounds such as 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2-tert-butylphenol, 2,6-diisopropylphenol, 2-methyl-6-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol, 4-(N,N-dimethylaminomethyl)-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 2-methyl-6-styrylphenol, 2,6-di-styryl-4-nonylphenol, and their analogs and homologs. Mixtures of two or more such mononuclear phenolic compounds are also suitable.

The preferred antioxidants for use in the compositions of this invention are methylene-bridged alkylphenols, and these can be used singly or in combinations with each other, or in combinations with sterically-hindered unbridged phenolic compounds. Illustrative methylene bridged compounds include 4,4 min -methylenebis(6-tert-butyl-o-cresol), 4,4 min -methylenebis-(2-tert-amyl-o-cresol), 2,2 min -methylenebis(4-methyl-6-tert-butylphenol), 4,4 min -methylenebis(2,6-di-tert-butylphenol), and similar compounds. Particularly preferred are mixtures of methylene-bridged alkylphenols such as are described in U.S. Pat. No. 3,211,652.

Amine antioxidants, especially oil-soluble aromatic secondary amines can also be used in the compositions of this invention. Whilst aromatic secondary monoamines are preferred, aromatic secondary polyamines are also suitable. Illustrative aromatic secondary monoamines include diphenylamine, alkyl diphenylamines containing 1 or 2 alkyl substituents each having up to about 16 carbon atoms, phenyl-alpha -naphthylamine, phenyl- beta -naphthylamine, alkyl- or aralkyl-substituted phenyl- alpha -naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, alkyl- or aralkyl-substituted phenyl- beta -naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, and similar compounds.

A preferred type of aromatic amine antioxidant is an alkylated diphenylamine of the general formula EMI97.1 wherein R1 is an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms) and R2 is a hydrogen atom or an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms). Most preferably, R1 and R2 are the same. One such preferred compound is available commercially as Naugalube 438L, a material which is understood to be predominantly a 4,4 min -dinyldiphenylamine (i.e., bis(4-nonylphenyl)amine) wherein the nonyl groups are branched.

Another useful type of antioxidant for inclusion in the compositions of this invention is comprised to one or more liquid, partially sulfurized phenolic compounds such as are prepared by reacting sulfur monochloride with a liquid mixture of phenols — at least about 50 weight percent of which mixture of phenols is composed of one or more reactive, hindered phenols — in proportions to provide from about 0.3 to about 0.7 gram atoms of sulfur monochloride per mole of reactive, hindered phenol so as to produce a liquid product. Typical phenol mixtures useful in making such liquid product compositions include a mixture containing by weight about 75% of 2,6-di-tert-butylphenol, about 10% of 2-tert-butylphenol, about 13% of 2,4,6-tri-tert-butylphenol, and about 2% of 2,4-di-tert-butylphenol. The reaction is exothermic and thus is preferably kept within the range of about 15 DEG C to about 70 DEG C, most preferably between about 40 DEG C to about 60 DEG C.

Mixtures of different antioxidants can also be used. One suitable mixture is comprised of a combination of (i) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated monohydric phenols which is in the liquid state at 25 DEG C, (ii) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated methylene-bridged polyphenols, and (iii) at least one bis(4-alkyl-phenyl)amine wherein the alkyl group is a branched alkyl group having 8 to 12 carbon atoms, the proportions of (i), (ii) and (iii) on a weight basis falling in the range of 3.5 to 5.0 parts of component (i) and 0.9 to 1.2 parts of component (ii) per part by weight of component (iii).

The lubricating compositions of this invention preferably contain 0.01 to 1.0% by weight, more preferably 0.05 to 0.7% by weight, of one or more sterically-hindered phenolic antioxidants of the types described above. Alternatively or additionally the lubricants of this invention may contain 0.01 to 1.0% by weight, more preferably 0.05 to 0.7% by weight of one or more aromatic amine antioxidants of the types described above.

#### Corrosion Inhibitors.

It is also preferred pursuant to this invention to employ in the lubricant compositions and additive concentrates a suitable quantity of a corrosion inhibitor. This may be a single compound or a mixture of compounds having the property of inhibiting corrosion of metallic surfaces.

One type of such additives are inhibitors of copper corrosion. Such compounds include thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercaptopbenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercaptop-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercaptop-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-(bis)hydrocarbyldithio)-1,3,4-thiadiazoles. The preferred compounds are the 1,3,4-thiadiazoles, a number of which are available as articles of commerce. Such compounds are generally synthesized from hydrazine and carbon disulfide by known procedures. See for example U.S. Pat. Nos. 2,765,289; 2,749,311; 2,760,933; 2,850,453; 2,910,439; 3,663,561; 3,862,798; and 3,840,549.

Other types of corrosion inhibitors suitable for use in the compositions of this invention include dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available from various commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humco Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Emery Chemicals. Another useful type of corrosion inhibitor for use in the practice of this invention are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; and the like. Materials of these types are well known to those skilled in the art and a number of such materials are available as articles of commerce.

Other useful corrosion inhibitors are aminosuccinic acids or derivatives thereof represented by the formula: EMI99.1 wherein each of R<1>, R<2>, R<5>, R<6> and R<7> is, independently, a hydrogen atom or a hydrocarbyl group containing 1 to 30 carbon atoms, and wherein each of R<3> and R<4> is, independently, a hydrogen atom, a hydrocarbyl group containing 1 to 30 carbon atoms, or an acyl group containing from 1 to 30 carbon atoms. The groups R<1>, R<2>, R<3>, R<4>, R<5>, R<6> and R<7>, when in the form of hydrocarbyl groups, can be, for example, alkyl, cycloalkyl or aromatic containing groups. Preferably R<1> and R<5> are the same or different straight-chain or branched-chain hydrocarbon radicals containing 1-20 carbon atoms. Most preferably, R<1> and R<5> are saturated hydrocarbon radicals containing 3-6 carbon atoms. R<2>, either R<3> or R<4>, R<6> and R<7>, when in the form of hydrocarbyl groups, are preferably the same or different straight-chain or branched-chain saturated hydrocarbon radicals. Preferably a dialkyl ester of an aminosuccinic acid is used in which R<1> and R<5> are the same or different alkyl groups containing 3-6 carbon atoms, R<2> is a hydrogen atom, and either R<3> or R<4> is an alkyl group containing 15-20 carbon atoms or an acyl group which is derived from a saturated or unsaturated carboxylic acid containing 2-10 carbon atoms.

Most preferred of the aminosuccinic acid derivatives is a dialkylester of an aminosuccinic acid of the above formula wherein R<1> and R<5> are isobutyl, R<2> is a hydrogen atom, R<3> is octadecyl and/or octadecenyl and R<4> is 3-carboxy-1-oxo-2-propenyl. In such ester R<6> and R<7> are most preferably hydrogen atoms.

The lubricant compositions of this invention most preferably contain from 0.005 to 0.5% by weight, and especially from 0.01 to 0.2% by weight, of one or more corrosion inhibitors and/or metal deactivators of the type described above.

#### Antifoam Agents.

Suitable antifoam agents include silicones and organic polymers such as acrylate polymers. Various antifoam agents are described in *Foam Control Agents* by H. T. Kerner (Noyes Data Corporation, 1976, pages 125-176). Mixtures of silicone-type antifoam agents such as the liquid dialkyl silicone polymers with various other substances are also effective. Typical of such mixtures are silicones mixed with an acrylate polymer, silicones mixed with one or more amines, and silicones mixed with one or more amine carboxylates.

#### Neutral Metal-Containing Detergents.

For some applications such as crankcase lubricants for diesel engines, it is desirable to include an oil-soluble neutral metal-containing detergent in which the metal is an alkali metal or an alkaline earth metal. Combinations of such detergents can also be employed. The neutral detergents of this type are those which contain an essentially stoichiometric equivalent quantity of metal in relation to the amount of acidic moieties present in the detergent. Thus in general, the neutral detergents will have a TBN of up to about 50.

The acidic materials utilized in forming such detergents include carboxylic acids, salicylic acids, alkylphenols, sulfonic acids, sulfurized alkylphenols, and the like. Typical detergents of this type and/or methods for their preparation are known and reported in the literature. See for example U.S. Pat. Nos. 2,001,108; 2,081,075; 2,095,538; 2,144,078; 2,163,622; 2,180,697; 2,180,698; 2,180,699; 2,211,972; 2,223,127; 2,228,654; 2,228,661; 2,249,626; 2,252,793; 2,270,183; 2,281,824; 2,289,795; 2,292,205; 2,294,145; 2,321,463; 2,322,307; 2,335,017; 2,336,074; 2,339,692; 2,356,043; 2,360,302; 2,362,291; 2,399,877; 2,399,878; 2,409,687; and 2,416,281. A number of such compounds are available as articles of commerce, such as for example, HiTEC TM 614 additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.).

#### Supplemental Antiwear and/or Extreme Pressure Additives.

For certain applications such as use as gear oils, the compositions of this invention will preferably contain one or more oil-soluble supplemental antiwear and/or extreme pressure additives. These comprise a number of well known classes of materials including, for example, sulfur-containing additives, esters of boron acids, esters of phosphorus acids, amine salts of phosphorus acids and acid esters, higher carboxylic acids and derivatives thereof, chlorine-containing additives, and the like.

Typical sulfur-containing antiwear and/or extreme pressure additives include dihydrocarbyl polysulfides; sulfurized olefins; sulfurized fatty acid esters of both natural (e.g. sperm oil) and synthetic origins; trithiones; thienyl derivatives; sulfurized terpenes; sulfurized oligomers of C2-C8 mono-olefins; xanthates of alkanols and other organo-hydroxy compounds such as phenols; thiocarbamates made from alkyl amines and other organo amines; and sulfurized Diels-Alder adducts such as those disclosed in U.S. reissue patent Re 27,331. Specific examples include sulfurized polyisobutene of Mn 1,100, sulfurized isobutylene, sulfurized triisobutene, dicyclohexyl disulfide, diphenyl and dibenzyl disulfide, di-tert-butyl trisulfide, and dinonyl trisulfide, among others.

Esters of boron acids which may be used include borate, metaborate, pyroborate and baborate esters of monohydric and/or polyhydric alcohols and/or phenols, such as trioctyl borate, tridecyl borate, 2-ethylhexyl pyroborate, isoamyl metaborate, trixylyl borate, (butyl)(2,4-hexanediy)borate, and the like.

Typical esters of phosphorus acids which may be used as antiwear and/or extreme pressure additives include trihydrocarbyl phosphites, phosphonates and phosphates, and dihydrocarbyl phosphites; such as tricresyl phosphate, tributyl phosphite, tris(2-chloroethyl)phosphate and phosphite, dibutyl trichloromethyl phosphonates, di(n-butyl)phosphite, triphenyl phosphite, and tolyl phosphinic acid dipropyl ester.

Among the amine salts of phosphorus acids and phosphorus acid-esters which can be employed are amine salts of partially esterified phosphoric, phosphorous, phosphonic, and phosphinic acids and their partial or total thio analogs such as partially esterified mono thiophosphoric, dithiophosphoric, trithiophosphoric and tetrathiophosphoric acids; amine salts of phosphonic acids and their thio analogs; and the like. Specific examples include the dihexylammonium salt of dodecylphosphoric acid, the diethyl hexyl ammonium salt of dioctyl dithiophosphoric acid, the octadecylammonium salt of dibutyl thiophosphoric acid, the dilaurylammonium salt of 2-ethylhexylphosphoric acid, the dioleyl ammonium salt of butane phosphonic acid, and analogous compounds.

Higher carboxylic acids and derivatives which can be used as antiwear and/or extreme pressure additives

are illustrated by fatty acids, dimerized and trimerized unsaturated natural acids (e.g., linoleic) and esters, amine, ammonia, and metal (particularly lead) salts thereof, and amides and imidazoline salt and condensation products thereof, oxazolines, and esters of fatty acids, such as ammonium di-(linoleic) acid, lard oil, oleic acid, animal glycerides, lead stearate, etc.

Suitable chlorine-containing additives include chlorinated waxes of both the paraffinic and microcrystalline type, polyhaloaromatics such as di- and trichlorobenzene, trifluoromethyl naphthalenes, perchlorobenzene, pentachlorophenol and dichloro diphenyl trichloroethane. Also useful are chlorosulfurized olefins and olefinic waxes and sulfurized chlorophenyl methyl chlorides and chloroxanthates. Specific examples include chlorodibenzyl disulfide, chlorosulfurized polyisobutene of Mn 600, chlorosulfurized pinene and chlorosulfurized lard oil.

#### Supplemental Ashless Dispersants.

If desired, the compositions of this invention can include one or more supplemental ashless dispersants in order to supplement the dispersancy contributed by component b). The supplemental ashless dispersant(s) differ from component b) in that the supplemental ashless dispersant(s) are not phosphorylated and boronated in the manner of component b). The supplemental ashless dispersant(s) can, nevertheless, be a phosphorylated or boronated ashless dispersant formed by using procedures of the types described herein for use in forming component b) or by using procedures of the types conventionally employed for producing by conventional technology ashless dispersants containing phosphorus or boron. For example, the supplemental ashless dispersant can be a basic nitrogen-containing and/or hydroxyl-containing ashless dispersant which has been heated with either one or more inorganic or one or more organic phosphorus compounds, or a combination of one or more inorganic and one or more organic phosphorus compounds.

Thus, the supplemental ashless dispersant(s) which may be used in the compositions of this invention can be any of the basic nitrogen-containing and/or hydroxyl group-containing ashless dispersants of the type referred to hereinabove in connection with the preparation of component b). Use can therefore be made of any of the carboxylic dispersants and/or any of the hydrocarbyl polyamine dispersants and/or any of the Mannich polyamine dispersants and/or any of the polymeric polyamine dispersants referred to hereinabove. Other ashless dispersants which can be included in the compositions of this invention are imidazoline dispersants which can be represented by the formula: EMI104.1 wherein R1 represents a hydrocarbon group having 1 to 30 carbon atoms, e.g. an alkyl or alkenyl group having 7 to 22 carbon atoms, and R2 represents a hydrogen atoms or a hydrocarbon radical of 1 to 22 carbon atoms, or an aminoalkyl, acylaminoalkyl or hydroxyalkyl radical having 2 to 50 carbon atoms. Such long-chain alkyl (or long-chain alkenyl) imidazoline compounds may be made by reaction of a corresponding longchain fatty acid (of formula R1-COOH), for example oleic acid, with an appropriate polyamine. The imidazoline formed is then ordinarily called, for example, oleylimidazoline where the radical R1 represents the oleyl residue of oleic acid. Other suitable alkyl substituents in the 2- position of these imidazolines include undecyl, heptadecyl, lauryl and erucyl. Suitable N-substituents of the imidazolines (i.e. radicals R2) include hydrocarbyl groups, hydroxyalkyl groups, aminoalkyl groups, and acylaminoalkyl groups. Examples of these various groups include methyl, butyl, decyl, cyclohexyl, phenyl, benzyl, tolyl, hydroxyethyl, aminoethyl, oleylaminoethyl and stearylarninoethyl.

Another class of ashless dispersant which can be incorporated in the compositions of this invention are the products of reaction of an ethoxylated amine made by reaction of ammonia with ethylene oxide with a carboxylic acid of 8 to 30 carbon atoms. The ethoxylated amine may be, for example, mono-, di- or triethanolamine or a polyethoxylated derivative thereof, and the carboxylic acid may be, for example, a straight or branched chain fatty acid of 10 to 22 carbon atoms, a naphthenic acid, a resinic acid or an alkyl aryl carboxylic acid.

Still another type of ashless dispersants which can be used in the practice of this invention are the alpha-olefin-maleimide copolymers such as are described in U.S. Pat. No. 3,909,215. Such copolymers are alternating copolymers of N-substituted maleimides and aliphatic alpha-olefins of from 8 to 30 carbon atoms. The copolymers may have an average of 4 to 20 maleimide groups per molecule. The substituents on the nitrogen of the maleimide may be the same or different and are organic radicals composed essentially of carbon, hydrogen and nitrogen having a total of 3 to 60 carbon atoms. A commercially available material which is highly suitable for use in this invention is Chevron OFA 425B, and this material is believed to be or comprise an alpha-olefin maleimide copolymer of the type described in U.S. Pat. No. 3,909,215.

The above and many other types of ashless dispersants can be utilized either singly or in combination in the compositions of this invention, provided of course that they are compatible with the other additive components being employed and are suitably soluble in the base oil selected for use.

### Pour Point Depressants.

Another useful type of additive included in compositions of this invention is one or more pour point depressants. The use of pour point depressants in oil-base compositions to improve the low temperature properties of the compositions is well known to the art. See, for example, the books Lubricant Additives by C. V. Smalheer and R. Kennedy Smith (Lezies-Hiles Co. Publishers, Cleveland, Ohio, 1967); Gear and Transmission Lubricants by C. T. Boner (Reinhold Publishing Corp., New York, 1964); and Lubricant Additives by M. W. Ranney (Noyes Data Corporation, New Jersey, 1973). Among the types of compounds which function satisfactorily as pour point depressants in the compositions of this invention are polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, and vinyl carboxylate polymers. Also useful as pour point depressants are terpolymers made by polymerizing a dialkyl fumarate, vinyl ester of a fatty acid and a vinyl alkyl ether. Techniques for preparing such polymers and their uses are disclosed in U.S. Pat. No. 3,250,715. Generally, when they are present in the compositions of this invention, the pour point depressants (on an active content basis) are present in amounts within the range of 0.01 to 5, and more often within the range of 0.01 to 1, weight percent of the total composition.

### Viscosity Index Improvers.

Depending upon the viscosity grade required, the lubricant compositions can contain up to 15 weight percent of one or more viscosity index improvers (excluding the weight of solvent or carrier fluid with which viscosity index improvers are often associated as supplied). Among the numerous types of materials known for such use are hydrocarbon polymers grafted with, for example, nitrogen-containing polymers, olefin polymers such as polybutene, ethylene-propylene copolymers, hydrogenated polymers and copolymers and terpolymers of styrene with isoprene and/or butadiene, polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate; post-grafted polymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine; styrene/maleic anhydride polymers post-treated with alcohols and/or amines, and the like.

Dispersant viscosity index improvers, which combine the activity of dispersants and viscosity index improvers, suitable for use in the compositions of this invention are described, for example, in U.S. Pat. Nos. 3,702,300; 4,068,056; 4,068,058; 4,089,794; 4,137,185; 4,146,489; 4,149,984; 4,160,739; and 4,519,929.

### Friction Modifiers.

These materials, sometimes known as fuel economy additives, include such substances as the alkyl phosphonates as disclosed in U.S. Pat. No. 4,356,097, aliphatic hydrocarbyl-substituted succinimides derived from ammonia or alkyl monoamines as disclosed in European Patent Publication No. 20037, dimer acid esters as disclosed in U.S. Pat. No. 4,105,571, oleamide, and the like. Such additives, when used are generally present in amounts of 0.1 to 5 weight percent. Glycerol oleates are another example of fuel economy additives and these are usually present in very small amounts, such as 0.05 to 0.2 weight percent based on the weight of the formulated oil.

Other suitable friction modifiers include aliphatic amines or ethoxylated aliphatic amines, aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, etc., wherein the aliphatic group usually contains above about eight carbon atoms so as to render the compound suitably oil soluble.

A desirable friction modifier additive combination which may be used in the practice of this invention is described in European Patent Publication No. 389,237. This combination involves use of a long chain succinimide derivative and a long chain amide.

### Seal Swell Agents.

Additives may be introduced into the compositions of this invention in order to improve the seal performance (elastomer compatibility) of the compositions. Known materials of this type include dialkyl

diesters such as dioctyl sebacate, aromatic hydrocarbons of suitable viscosity such as Panasol AN-3N, products such as Lubrizol 730, polyol esters such as Emery 2935, 2936, and 2939 esters from the Emery Group of Henkel Corporation and Hatcol 2352, 2962, 2925, 2938, 2939, 2970, 3178, and 4322 polyol esters from Hatco Corporation. Generally speaking the most suitable diesters include the adipates, azelates, and sebacates of C8-C13 alkanols (or mixtures thereof), and the phthalates of C4-C13 alkanols (or mixtures thereof). Mixtures of two or more different types of diesters (e.g., dialkyl adipates and dialkyl azelates, etc.) can also be used. Examples of such materials include the n-octyl, 2-ethylhexyl, isodecyl, and tridecyl diesters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and tridecyl diesters of phthalic acid.

## Base Oils.

The additive combinations of this invention can be incorporated in a wide variety of lubricants and functional fluids in effective amounts to provide suitable active ingredient concentrations. The base oils not only can be hydrocarbon oils of lubricating viscosity derived from petroleum (or tar sands, coal, shale, etc.), but also can be natural oils of suitable viscosities such as rapeseed oil, etc., and synthetic oils such as hydrogenated polyolefin oils; poly- alpha -olefins (e.g., hydrogenated or unhydrogenated alpha -olefin oligomers such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; polysilicones; fluorohydrocarbon oils; and mixtures of mineral, natural and/or synthetic oils in any proportion, etc. The term "base oil" for this disclosure includes all the foregoing.

The additive combinations of this invention can thus be used in lubricating oil and functional fluid compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, gear oils, hydraulic oils, cutting oils, etc., in which the base oil of lubricating viscosity is a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof, e.g. a mixture of a mineral oil and a synthetic oil.

Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Middle East, North Sea and the like. Standard refinery operations may be used in processing the mineral oil. Among the general types of petroleum oils useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques which are widely known by those skilled in the art.

As is noted above, the base oil can consist essentially of or comprise a portion of one or more synthetic oils. Among the suitable synthetic oils are homo- and inter-polymers of C2-C12 olefins, carboxylic acid esters of both monoalcohols and polyols, polyethers, silicones, polyglycols, silicates, alkylated aromatics, carbonates, thiocarbonates, orthoformates, phosphates and phosphites, borates and halogenated hydrocarbons. Representative of such oils are homo- and interpolymers of C2-C12 monoolefinic hydrocarbons, alkylated benzenes (e.g., dodecyl benzenes, didodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di-(2-ethylhexyl)benzenes, wax-alkylated naphthalenes); and polyphenyls (e.g., biphenyls, terphenyls).

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of synthetic oils. These are exemplified by the oils prepared through polymerization of alkylene oxides such as ethylene oxide or propylene oxide, and the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl polyisopropylene-glycol ether having an average-molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500) or mono- and poly-carboxylic esters thereof, for example, the acetic acid ester, mixed C3-C6 fatty acid esters, or the C13 Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)adipate, didodecyl adipate, di(2-ethylhexyl)sebacate, dilauryl sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisoctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, di(eicosyl)sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters which may be used as synthetic oils also include those made from C3-C12 monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol and

dipentaerythritol. Trimethylol propane tripelargonate and pentaerythritol tetracaproate serve as examples.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl)silicate, poly(methyl)siloxanes, and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, triphenyl phosphite, and diethyl ester of decane phosphonic acid).

Also useful as base oils or as components of base oils are hydrogenated or unhydrogenated liquid oligomers of C6-C16 alpha-olefins, such as hydrogenated or unhydrogenated oligomers formed from 1-decene. Methods for the production of such liquid oligomeric 1-alkene hydrocarbons are known and reported in the literature. See for example U.S. Pat. Nos. 3,749,560; 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822. Additionally, hydrogenated 1-alkene oligomers of this type are available as articles of commerce, for example, under the trade designations ETHYLFLO 162, ETHYLFLO 164, ETHYLFLO 166, ETHYLFLO 168, ETHYLFLO 170, ETHYLFLO 174, and ETHYLFLO 180 poly-alpha-olefin oils (Ethyl Corporation; Ethyl S.A.; Ethyl Canada Limited). Blends of such materials can also be used in order to adjust the viscometrics of the given base oil. Suitable 1-alkene oligomers are also available from other suppliers. As is well known, hydrogenated oligomers of this type contain little, if any, residual ethylenic unsaturation.

Preferred oligomers are formed by use of a Friedel-Crafts catalyst (especially boron trifluoride promoted with water or a C1-20 alkanol) followed by catalytic hydrogenation of the oligomer so formed using procedures such as are described in the foregoing U.S. patents.

Other catalyst systems which can be used to form oligomers of 1-alkene hydrocarbons, which, on hydrogenation, provide suitable oleaginous liquids include Ziegler catalysts such as ethyl aluminum sesquichloride with titanium tetrachloride, aluminum alkyl catalysts, chromium oxide catalysts on silica or alumina supports and a system in which a boron trifluoride catalyst oligomerization is followed by treatment with an organic peroxide.

It is also possible in accordance with this invention to utilize blends of one or more liquid hydrogenated 1-alkene oligomers in combination with other oleaginous materials having suitable viscosities, provided that the resultant blend has suitable compatibility and possesses the physical properties desired.

Typical natural oils that may be used as base oils or as components of the base oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and the like. Such oils may be partially or fully hydrogenated, if desired.

The fact that the base oils used in the compositions of this invention may be composed of (i) one or more mineral oils, (ii) one or more synthetic oils, (iii) one or more natural oils, or (iv) a blend of (i) and (ii), or (i) and (iii), or (ii) and (iii), or (i), (ii) and (iii) does not mean that these various types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain compositions for the specific properties they possess such as high temperature stability, non-flammability or lack of corrosivity towards specific metals (e.g. silver or cadmium). In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the various types of base oils discussed above may be used in the compositions of this invention, they are not necessarily functional equivalents of each other in every instance.

#### Proportions and Concentrations

In general, the components of the additive compositions of this invention are employed in the oleaginous liquids (e.g., lubricating oils and functional fluids) in minor amounts sufficient to improve the performance characteristics and properties of the base oil or fluid. The amounts will thus vary in accordance with such factors as the viscosity characteristics of the base oil or fluid employed, the viscosity characteristics desired in the finished product, the service conditions for which the finished product is intended, and the performance characteristics desired in the finished product. However, generally speaking, the following concentrations (weight percent) of the components (active ingredients) in the base oils or fluids are illustrative: EMI113.1

The concentrations (weight percent of active ingredient) of typical optional ingredients in the oleaginous liquid compositions of this invention are generally as follows: EMI113.2

It will be appreciated that the individual components a) and b), preferably component c) as well, and also any and all auxiliary components employed, can be separately blended into the base oil or fluid or can be

blended therein in various subcombinations, if desired. Moreover, such components can be blended in the form of separate solutions in a diluent. Except for viscosity index improvers and/or pour point depressants (which are usually blended apart from other components), it is preferable to blend the components used in the form of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate.

The additive concentrates of this invention will contain components a) and b), and preferably component c), in amounts proportioned to yield finished oil or fluid blends consistent with the concentrations tabulated above. In most cases, the additive concentrate will contain one or more diluents such as light mineral oils, to facilitate handling and blending of the concentrate. Thus concentrates containing up to 50% by weight of one or more diluents or solvents can be used.

The oleaginous liquids provided by this invention can be used in a variety of applications. For example, they can be employed as crankcase lubricants, gear oils, hydraulic fluids, manual transmission fluids, automatic transmission fluids, cutting and machining fluids, brake fluids, shock absorber fluids, heat transfer fluids, quenching oils, transformer oils, and the like. The compositions are particularly suitable for use as crankcase lubricants for spark ignition (gasoline) engines, and compression ignition (diesel) engines.

#### Blending

The formulation or blending operations are relatively simple and involve mixing together in a suitable container or vessel, using a dry, inert atmosphere where necessary or desirable, appropriate proportions of the selected ingredients. Those skilled in the art are cognizant of and familiar with the procedures suitable for formulating and blending additive concentrates and lubricant compositions. Usually the order of addition of components to the blending tank or vessel is not critical provided of course, that the components being blended at any given time are not incompatible with each other. Agitation such as with mechanical stirring equipment is desirable to facilitate the blending operation. Frequently it is helpful to apply sufficient heat to the blending vessel during or after the introduction of the ingredients thereto, so as to maintain the temperature at, say, 40-60 DEG C. Similarly, it is sometimes helpful to preheat highly viscous components to a suitable temperature even before they are introduced into the blending vessel in order to render them more fluid and thereby facilitate their introduction into the blending vessel and render the resultant mixture easier to stir or blend. Naturally the temperatures used during the blending operations should be controlled so as not to cause any significant amount of thermal degradation or unwanted chemical interactions.

When forming the lubricant compositions of this invention, it is usually desirable to introduce the additive ingredients into the base oil with stirring and application of mildly elevated temperatures, as this facilitates the dissolution of the components in the oil and achievement of product uniformity.

The practice and advantages of this invention are still further illustrated by the following examples in which all parts and percentages are by weight unless otherwise specifically indicated. In these examples, the weights of the various ingredients are on an "as received" basis — i.e., the weights include solvents or diluents which are in the products as supplied.

#### EXAMPLE 1

A crankcase lubricating oil of this invention containing 0.11% phosphorus and 0.02% boron is formed by blending together the following components: EMI115.1 EMI116.1

#### EXAMPLE 2

Using the same ingredients as in Example 1 except where otherwise indicated, a crankcase lubricating oil of this invention containing 0.13% phosphorus and 0.01% boron is formed by blending together the following components: EMI116.2 EMI117.1

#### EXAMPLE 3

The procedure of Example 2 is repeated except that component b) is prepared as in Example A-45 and is employed at a concentration of 2.970%. The amount of the base oil is thus 82.886%.

#### EXAMPLE 4

Using the same ingredients as in Example 1 except where otherwise indicated, a crankcase lubricating oil of this invention is formed by blending together the following components: EMI117.2 EMI118.1

#### EXAMPLE 5

Using the same ingredients as in Example 4 except where otherwise indicated, a crankcase lubricating oil of this invention is formed by blending together the following components: EMI118.2 EMI119.1

#### EXAMPLE 6

The procedures of Examples 4 and 5 are repeated except that in each case the sulfurized fatty ester is eliminated and replaced by a corresponding amount of process oil.  
)

#### EXAMPLE 7

The procedure of Example 4 is repeated using the same ingredients as therein specified except where otherwise indicated below: EMI119.2

#### EXAMPLE 8

The procedure of Example 5 is repeated using the same ingredients as therein specified except where otherwise indicated below: EMI119.3 EMI120.1

#### EXAMPLE 9

The procedures of Examples 7 and 8 are repeated except that in each case the sulfurized fatty ester is eliminated and replaced by a corresponding amount of process oil.

#### EXAMPLE 10

A synthetic lubricant of this invention is formed by blending together the following components in the amounts specified: EMI120.2 EMI121.1

#### EXAMPLE 11

The procedure of Example 10 is repeated except that component b) is prepared as in Example A-45 and is employed at a concentration of 5.940%, and the amount of process oil used is 1.560%.

#### EXAMPLE 12

The procedure of Example 10 is repeated using the same ingredients except as otherwise specified: EMI121.2 EMI122.1

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### EXAMPLE 13

The procedure of Example 12 is repeated using the same ingredients except where otherwise specified:  
EMI122.2

### EXAMPLE 14

An additive concentrate of this invention is formed by blending together the following components as identified in Example 1: EMI123.1

### EXAMPLE 15

An additive concentrate of this invention is formed by blending together the following components as identified in Example 3: EMI123.2

### EXAMPLE 16

An additive concentrate of this invention is formed by blending together the following components as identified in Example 4: EMI123.3

### EXAMPLE 17

An additive concentrate of this invention is formed by blending together the following components as identified in Example 5: EMI124.1

### EXAMPLE 18

An additive concentrate of this invention is formed by blending together the following components as identified in Example 4: EMI124.2

### EXAMPLE 19

An additive concentrate of this invention is formed by blending together the following components as identified in Example 7: EMI124.3 EMI125.1

### EXAMPLE 20

An additive concentrate of this invention is formed by blending together the following components as identified in Example 8: EMI125.2

### EXAMPLE 21

An additive concentrate of this invention is formed by blending together the following components:  
EMI125.3 EMI126.1 A lubricant composition of this invention is formed by blending the above concentrate and a viscosity index improver in a base oil as follows: EMI126.2

### EXAMPLE 22

An additive concentrate of this invention is formed by blending together the components as identified in Example 21 in the following proportions: EMI127.1 A lubricant composition of this invention is formed by blending the above concentrate and the viscosity index improver of Example XXI in a base oil composed of 63.2% Petro Canada 160 neutral oil and 15.8% Petro Canada 650 neutral oil as follows: EMI127.2

#### EXAMPLE 23

A crankcase lubricating oil of this invention is formed by blending together the following components: EMI127.3 EMI128.1

#### EXAMPLE 24

Using the same ingredients as in Example 23 except where otherwise indicated, a crankcase lubricating oil of this invention is formed by blending together the following components: EMI128.2 EMI129.1

#### EXAMPLE 25

The procedure of Example 24 is repeated except that component b) is prepared as in Example B-45 and is employed at a concentration of 2.970%. The amount of the base oil is thus 82.886%.

#### EXAMPLE 26

Using the same ingredients as in Example 23 except where otherwise indicated, a crankcase lubricating oil of this invention is formed by blending together the following components: EMI129.2 EMI130.1

#### EXAMPLE 27

Using the same ingredients as in Example 26 except where otherwise indicated, a crankcase lubricating oil of this invention is formed by blending together the following components: EMI130.2

#### EXAMPLE 28

The procedures of Examples 26 and 27 are repeated except that in each case the sulfurized fatty ester is eliminated and replaced by a corresponding amount of process oil.

#### EXAMPLE 29

The procedure of Example 26 is repeated using the same ingredients as therein specified except where otherwise indicated below: EMI131.1

#### EXAMPLE 30

The procedure of Example 27 is repeated using the same ingredients as therein specified except where otherwise indicated below: EMI131.2

#### EXAMPLE 31

The procedures of Examples 29 and 30 are repeated except that in each case the sulfurized fatty ester is eliminated and replaced by a corresponding amount of process oil.

**EXAMPLE 32**

A synthetic lubricant of this invention is formed by blending together the following components in the amounts specified: EMI132.1 EMI133.1

**EXAMPLE 33**

The procedure of Example 32 is repeated except that component b) is prepared as in Example B-45 and is employed at a concentration of 5.940%, and the amount of process oil used is 1.560%.

**EXAMPLE 34**

The procedure of Example 32 is repeated using the same ingredients except as otherwise specified:  
EMI133.2

**EXAMPLE 35**

The procedure of Example 34 is repeated using the same ingredients except where otherwise specified:  
EMI134.1

**EXAMPLE 36**

An additive concentrate of this invention is formed by blending together the following components as identified in Example 23: EMI134.2

**EXAMPLE 37**

An additive concentrate of this invention is formed by blending together the following components as identified in Example 25: EMI135.1

**EXAMPLE 38**

An additive concentrate of this invention is formed by blending together the following components as identified in Example IV: EMI135.2

**EXAMPLE 39**

An additive concentrate of this invention is formed by blending together the following components as identified in Example 27: EMI135.3

**EXAMPLE 40**

An additive concentrate of this invention is formed by blending together the following components as identified in Example 26: EMI136.1

**EXAMPLE 41**

An additive concentrate of this invention is formed by blending together the following components as identified in Example 29: EMI136.2

#### EXAMPLE 42

An additive concentrate of this invention is formed by blending together the following components as identified in Example 30: EMI136.3

#### EXAMPLE 43

An additive concentrate of this invention is formed by blending together the following components:  
EMI137.1 A lubricant composition of this invention is formed by blending the above concentrate and a viscosity index improver in a base oil as follows: EMI138.1

#### EXAMPLE 44

An additive concentrate of this invention is formed by blending together the components as identified in Example 43 in the following proportions: EMI138.2 A lubricant composition of this invention is formed by blending the above concentrate and the viscosity index improver of Example XXI in a base oil composed of 63.2% Petro Canada 160 neutral oil and 15.8% Petro Canada 650 neutral oil as follows: EMI139.1

The lubricating oil composition of Example 1 was subjected to the standard Sequence VE engine test procedure. The results of this evaluation are summarized in the following table, which also shows the American Petroleum Institute SG passing limits for the various parameters. EMI139.2

The antiwear advantages that can be achieved by the practice of this invention were further illustrated by a series of standard 4-Ball wear tests (40 kg load, 1800 rpm, 130 DEG F, 30 minute test length) on three lubricating oil compositions having the same total concentration of phosphorus therein. The compositions were identical to each other except that one such composition (Oil A) contained only zinc dialkyldithiophosphate as the phosphorus-containing component whereas another such composition (Oil B) contained a phosphorylated and boronated succinimide of this invention as the sole source of phosphorus. Oil C, a representative composition of this invention, contained the combination of both the same zinc dialkyldithiophosphate and the same phosphorylated and boronated succinimide dispersant. All compositions also contained the same concentration of overbased calcium sulfonate having a nominal TBN of 300. The makeup of these compositions was as follows:

##### Oil A

0.98 grams of zinc dialkyldithiophosphate<1>  
(1) HiTEC TM 685 Additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.)

1.85 grams of overbased calcium sulfonate<2>

(2) HiTEC TM 611 Additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.)

147.19 grams of mineral oil<3>

(3) Turbine 5 oil, a 100 Solvent Neutral refined mineral oil.

##### Oil B

10.02 grams of phosphorylated and boronated succinimide  
(4) Prepared as in Example A-44.

1.85 grams of overbased calcium sulfonate<2>

138.13 grams of mineral oil<3>

##### Oil C

0.48 grams of zinc dialkyldithiophosphate<1>  
5.01 grams of phosphorylated and boronated succinimide<4>

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1.85 grams of overbased calcium sulfonate<2>  
142.66 grams of mineral oil<3>

The results of these 4-Ball tests were as follows: EMI141.1

The ability of overbased alkali or alkaline earth metal-containing detergents to suppress copper corrosion was demonstrated by a series of tests employing varied proportions of components a), b), and c) in a base oil (Turbine 5 oil). These tests were conducted according to ASTM D-130 but under more severe conditions, viz., operation at 121 DEG C rather than at the standard temperature of 100 DEG C. In these tests component a) was HiTEC TM 665 additive (a zinc dialkyl dithiophosphate described above), component b) was formed as in Example A-44, and component c) was HiTEC TM 611 additive (an overbased calcium sulfonate). The compositions tested (weight percentages) and the results obtained therewith are tabulated below: EMI141.2

Another feature of this invention is that the particularly preferred phosphorylated and boronated alkenyl succinimides of polyethylene polyamines made from alkenyl succinic anhydrides (or like succinic acylating agents, such as the acid, acid halide, lower alkyl ester, lower alkyl-acid ester) in which the succination ratio (i.e., ratio of the average number of succinic groups per alkenyl group chemically bound in the acylating agent) is in the range of 1:1 to about 1.3::1 and in which the alkenyl group is derived from a polyolefin having a number average molecular weight in the range of about 600 to about 1,300 (preferably about 700 to about 1,200, and most preferably about 800 to about 1,100) when utilized in accordance with this invention can provide greater dispersancy than the same concentration or an even higher concentration of an analogous succinimide not containing boron or phosphorus or an analogous boronated succinimide made from a polyolefin of even higher molecular weight.

For example, a group of lubricant compositions made from different succinimide dispersants were subjected to a bench test simulating sludge performance in the Sequence VE engine tests. This test involves subjecting each lubricant to standard Hot Oil Oxidation Test (HOOT) conditions and determining the change in dielectric constant of the lubricants before and after the oxidation. On completion of the oxidation, the oxidized oil is mixed with a known amount of standard oxidized oil (a laboratory preparation) and diluted with a hydrotreated base stock. Turbidity measurements are then taken and then dielectric constant measurement, HOOT time and turbidity data, are combined into a single number for reporting and comparison purposes. A lower number indicates better anti-sludge properties.

The lubricant compositions subjected to this test each contained zinc dialkyl dithiophosphate and a succinimide dispersant, together with the remainder of the additive complement described in Example 11 above. The oils each contained 1.20% of the zinc dialkyl dithiophosphate (HiTEC TM 685 additive). The concentrations of the respective succinimides were adjusted such that the respective oils each contained 6.0% by weight of the active succinimide dispersant disregarding the amount of any boron-containing or phosphorus- and boron-containing species introduced into the succinimide by boronation or by phosphorylation and boronation.

The results of these tests were as follows: EMI143.1

Rendering these results all the more remarkable is the fact that in U.S. Pat. No. 4,873,004 it is pointed out that to achieve improved dispersancy properties it is necessary to have a molar ratio of succinic groups to alkenyl groups (sometimes referred to as the "succination ratio") of at least 1.4 when using succinimides made from polyamines such as tetraethylene pentamine and polyisobutylene succinic anhydrides having number average molecular weights in the range of 600 to 1,300. For example the patent shows in its Tables 3 and 4 that with succinimide derived from polyisobutylene of number average molecular weight of 950, maleic anhydride and tetraethylene pentamine, products having a succination ratio of 1.0 gave inferior results on dispersancy and varnish formation than corresponding succinimides in which the succination ratio was 1.8. Yet as shown hereinabove, a boronated and phosphorylated polyisobutylene succinimide with a succination ratio of about 1.18 made from polyisobutene of number average molecular weight of about 900, gave excellent results both on dispersancy and on wear prevention.

As used in the foregoing description, the term "oil-soluble" is used in the sense that the component in question has sufficient solubility in the selected base oil in order to dissolve therein at ordinary temperatures to a concentration at least equivalent to the minimum concentration specified herein for use of such component. Preferably, however, the solubility of such component in the selected base oil will be in excess of such minimum concentration, although there is no requirement that the component be soluble in the base oil in all proportions. As is well known to those skilled in the art, certain useful additives do not completely dissolve in base oils but rather are used in the form of stable suspensions or dispersions. Additives of this type can be employed in the compositions of this invention, provided they do not significantly interfere with the performance or usefulness of the composition in which they are employed.



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**Lubricating oil compositions, concentrates and the use thereof.**

## Claims of EP0493928

1. A lubricant or functional fluid composition or additive concentrate which comprises at least one oil of lubricating viscosity and at least the following components:
  - a) one or more oil-soluble metal hydrocarbyl dithiophosphates or dithiocarbamates; and
  - b) one or more oil-soluble additive compositions formed by a process which comprises heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with
    - (i) at least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing; or
    - (ii) at least one water-hydrolyzable organic phosphorus compound and water; and
    - (iii) at least one boron compound; such that a phosphorus- and boron-containing liquid composition is formed, and from which excessive water, if present, has been removed at least during or after heating with (ii), if used.
2. A composition as claimed in Claim 1 wherein component a) consists essentially of one or more oil-soluble zinc dihydrocarbyl dithiophosphates.
3. A composition as claimed in Claim 1 wherein component a) consists essentially of a combination of at least two oil-soluble zinc dialkyl dithiophosphates.
4. A composition as claimed in any of Claims 1 through 3 wherein component b) is further characterized in that said at least one ashless dispersant used in forming said phosphorus- and boron-containing liquid composition consists essentially of (1) at least one hydrocarbyl succinamide, or (2) at least one hydrocarbyl-substituted succinic ester-amide, or (3) at least one hydroxyester of hydrocarbyl succinic acid, or (4) at least one Mannich condensation product of hydrocarbyl-substituted phenol, formaldehyde and polyamine, or (5) at least one hydrocarbyl succinimide, or any combination of any two, or any three, or any four, or all five (1), (2), (3), (4) and (5).
5. A composition as claimed in any of Claims 1 through 3 wherein component b) is further characterized in that said at least one ashless dispersant used in forming said phosphorus- and boron-containing liquid composition consists essentially of at least one acyclic hydrocarbyl-substituted succinimide of a mixture of ethylene polyamines having an approximate overall composition falling in the range corresponding to diethylene triamine to pentaethylene hexamine.
6. A composition in accordance with any of Claims 1 through 5 wherein component b) is further characterized in that said at least one ashless dispersant used in forming said phosphorus- and boron-containing liquid composition consists essentially of at least one acyclic hydrocarbyl-substituted succinimide ashless dispersant having a succination ratio of 1:1 to about 1.3:1.  
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7. A composition in accordance with any of Claims 1 through 6 wherein component b) is further characterized in that said at least one ashless dispersant used in forming said phosphorus- and boron-containing liquid composition is comprised of at least one substituted succinimide in which the substituent is derived from a polyolefin having a number average molecular weight in the range of 500 to 5,000.
8. A composition as claimed in Claim 8 wherein said substituent is derived from polyisobutene having a number average molecular weight in the range of 700 to 2,500.
9. A composition as claimed in any of Claims 1 through 8 further comprising a minor proportion of at least one oil-soluble alkali or alkaline earth metal-containing detergent.
10. A composition as claimed in any of Claims 1 through 9 further comprising a minor proportion of at least one oil-soluble overbased alkali or alkaline earth metal-containing sulfonate.
11. A composition in accordance with any of Claims 1 through 10 wherein component b) is formed by heating (i) and (iii) thereof with said ashless dispersant, concurrently or sequentially in any order.
12. A method of operating an internal combustion engine having a crankcase containing a lubricating oil formulation, which method comprises utilizing as the lubricating oil formulation in said crankcase a lubricant composition according to any of Claims 1 through 11 hereof.
13. A method of operating a mechanical mechanism in which an elastomeric material is in contact with a lubricant or functional fluid, which method comprises utilizing as said lubricant or functional fluid a

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composition according to any of Claims 1 through 11 hereof.

14. A method according to Claim 13 wherein the elastomeric material comprises a fluoroelastomer.

15. A method of formulating a lubricant or functional fluid wherein a plurality of additive components are blended into an oil of lubricating viscosity characterized in that at least one oil-soluble zinc dihydrocarbyl dithiophosphate and at least one oil-soluble phosphorus- and boron-containing liquid composition are blended into said oil, said phosphorus- and boron-containing liquid composition having been prepared by a process which comprises heating at least one basic nitrogen-containing and/or hydroxyl-containing ashless dispersant concurrently or in any sequence with (i) at least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing; or (ii) at least one water-hydrolyzable organic phosphorus compound and water; and (iii) at least one boron compound; such that a phosphorus- and boron-containing liquid composition is formed, and from which excessive water, if present, has been removed at least during or after heating with (ii), if used.

16. A method according to Claim 15 wherein the total concentration of said at least one zinc dihydrocarbyl dithiophosphate and said phosphorus- and boron-containing liquid composition that is blended into said oil of lubricating viscosity is in the range of 0.111 to 251, preferably 0.3% to 17%, more preferably 0.8% to 11.4%, and most preferably 1.35 to 9.35% by weight based on the total weight of the lubricant or functional fluid composition.

17. A method according to Claim 15 or 16 wherein a portion or substantially all of said phosphorus- and boron-containing liquid composition is blended into said oil of lubricating viscosity concurrently with a portion or substantially all of said at least one oil-soluble zinc dihydrocarbyl dithiophosphate.

18. A method of formulating a lubricant or functional fluid wherein a selected amount of phosphorus in the form of one or more oil-soluble phosphorus-containing components is blended into an oil of lubricating viscosity, wherein said amount of phosphorus is made up at least in part of at least one zinc dihydrocarbyl dithiophosphate, and wherein said selected amount includes phosphorus in the form of at least one liquid oil-soluble composition formed by heating concurrently or in any sequence at least one ashless dispersant which contains basic nitrogen and/or at least one hydroxyl group with (i) at least one inorganic phosphorus acid or anhydride, or at least one partial or total sulfur analog thereof, or any combination of the foregoing; or (ii) at least one water-hydrolyzable organic phosphorus compound and water; and (iii) at least one boron compound; such that a phosphorus- and boron-containing liquid composition is formed, and from which excessive water, if present, has been removed at least during or after heating with (ii), if used.

19. A method according to any of Claims 15 through 18 wherein said at least one ashless dispersant used in forming said phosphorus- and boron-containing liquid composition consists essentially of at least one acyclic hydrocarbyl-substituted succinimide of a mixture of ethylene polyamines having an approximate overall composition falling in the range corresponding to diethylene triamine to pentaethylene hexamine; wherein said phosphorus- and boron-containing liquid composition is formed by heating (i) and (iii) thereof with said ashless dispersant, concurrently or sequentially in any order; and wherein there is also blended into said oil of lubricating viscosity a minor proportion of (1) at least one oil-soluble overbased alkali metal-containing detergent or (2) at least one oil-soluble overbased alkaline earth metal-containing detergent, or a combination of (1) and (2).